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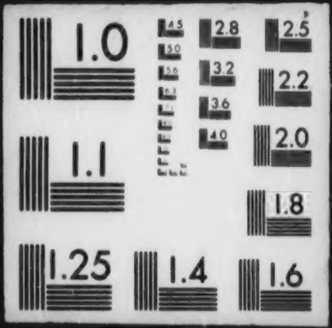

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AIR POLLUTION CONTROL ENGINEERING AND COST STUDY OF THE PAINT AND VARNISH INDUSTRY

AIR RESOURCES, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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16. ABSTRACT

Under this contract, a comprehensive study was conducted of the Paint and Varnish Industry and its relationship to the pollution of our environment. The report presents a description of the industry, its method of operation and the chemical processes utilized. Also presented are comprehensive industry statistics including type, size and location of present day plants and past, present and projected industry trends. In addition, the following environmental and economic information is presented: types and quantities of air pollution emissions and their geographical distribution; the effect of operations on air pollution emissions; the impact of emissions on air quality; the type and effectiveness of existing control technology; performance and costs of best control technology; the economic impact of the use of best control by the industry; emission measurement techniques and problems; inspection procedures to determine compliance with air pollution regulations; and areas of needed research and development. The manufacture of various pigments is included as part of the Paint and Varnish Industry study. A three page bibliography is included in the report. The manufacture of TiO_2 was studied in detail.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Air Pollution Control Equipment Scrubbers Condensation Resins Zinc Oxide Iron Oxides Titanium Dioxide Cost Analysis Hydrocarbons	Resin Production Paint Production Varnish Production Particulates Solvent Emissions Cadmium Pigment Chrome Pigment Thermal Afterburners, Catalytic Afterburner	7/A, 7/B 11/I 13/B, 13/I

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Prepared for

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Office of Air Quality Planning and Standards
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June 1974

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This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - as supplies permit - from the Air Pollution Technical Information Center, Environmental Protection Agency, Research Triangle Park, North Carolina 27711, or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22151.

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FOREWARD

This air pollution control engineering and cost study of the paint and varnish industry was conducted under Contract No. 68-02-0259 for the office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Industrial Studies Branch. The study is being conducted by the EPA under public law No. 91604, Clean Air Amendments of 1970. This law permits that industry studies be conducted to obtain information as outlined below.

Section 111

This section of the law requires that future growth of industry should contribute a minimum impact on the quality of air. It provides that the Federal Government will review the capabilities for controlling air pollution in industry and that certain designed source categories will be required to install the best emission control systems.

One source of information used to develop performance standards required to ensure best emission control evolves from the type of industry study provided herein. Trade associations of the industry are consulted during the establishment of proposed standards. Plants which utilize the best control techniques are examined and source tested. Test data and economics of control are considered in the setting of standards. Proposed standards are then reviewed at open meetings by industry, governmental agencies and other interested parties.

Section 114

This section of the law provides to the Environmental Protection Agency the right to such information as it deems necessary for establishing standards. Industry cannot withhold information from the EPA on the grounds that it is considered confidential. In accordance with title 18 of Section 1905 in the United States Code, if the EPA requires information which in a company's opinion is a trade secret then the company may submit, along with the information, a request that the data be maintained confidential. This request must include reasons why the data is confidential. EPA Legal Council will review the request and will render a decision as to whether it should be held confidential and will so notify the company. If the decision is made that it will not be held confidential, the company has 30 days to consider legal action.

The three general categories of information requested of industry are:

a. Emission data
b. Economic information
c. Process information

The Clean Air Act clearly states that emission data is public information and will be made available upon request. Process data may be held confidential only if the information can be shown to constitute a trade secret. The Office of General Council must rule on any process data considered to be confidential by a company based on the reasons submitted with the request for confidentiality. With a determination that certain information is a trade secret, such information will be used for setting performance standards, but the data will not be released to the general public. Such information may be used in summaries or in legal action if required by the Federal Government for carrying out the purpose of the act.

Section 113 — Federal Enforcement Powers

Most state agencies will in all likelihood enforce new source performance standards; however, the federal agency has the right to intervene under this section of the law. Where a state is not prepared to enforce the standards, the Federal Government will have the responsibility.

The paint and varnish industry shall be considered to consist of all phases of operations normally found located in plants engaged in the manufacture of paints, lacquers, varnishes, etc. (Standard Industrial Classification 2851). The study shall include the storing, packaging, shipping, handling, mixing, thinning, grinding, cooking, and other processing necessary in the manufacturing of paint and varnish products from raw materials through finished products. The manufacture of resins by both paint manufacturers and raw material suppliers shall be included. The manufacture and processing of a number of pigments will also be included in this study. The study of the pigments will not be as detailed as the paint and varnish study and it will be limited to those manufacturing processes which contribute significantly to environmental air pollution. The study will develop the following information on the paint and varnish industry:

1. An industry description which incorporates all industry information relevant to emission problems, including comprehensive industry statistics, emission sources, types of emissions as well as emission quantities as related to operational factors.

2. A study of technical and economic information on the best control systems. An assessment of the economic impact on the entire industry if these best controls were applied to new and existing plants.

3. Identification of technological and economic deficiencies in air pollution control technology within the paint and varnish industry. Analysis of those deficiencies that restrict additional reduction of emissions along with recommendations of R&D Programs that would produce the greatest improvement in control technology.

Resulting reports will include past and projected production data, geographical location of paint plants, types and amounts of air pollutant emissions, control techniques, performance and costs of existing and best control technology, impact of emissions on air quality, inspection procedures to determine compliance with air pollution control regulations, and areas of needed research and development.

Techniques used in the study included literature searches, plant visits, source testing and comprehensive industry questionnaires. Two subcontractors were also employed. These subcontracts are discussed below.

The Industrial Gas Cleaning Institute (IGCI) was subcontracted to supply detailed capital, installation and operating cost information for air pollution equipment used by the coating industry.

The Sherwin-Williams Company was subcontracted to supply capital and operating cost information for the model plant developed for this study. These two subcontracts are discussed in more detail in Chapter 7, "ECONOMICS OF EMISSION CONTROL".

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The work reported herein has been reviewed by an Industry Advisory Committee comprised of the members listed below. The authors wish to gratefully acknowledge the technical review, advice and assistance they provided throughout the period of this contract.

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Hirt Combustion Engineers — Equipment Manufacturer

The assistance of other organizations and companies who supplied assistance in completion of this study are too numerous to list and are also gratefully acknowledged, particularly those who filled out questionnaires, supplied data, provided time for visits, and permitted source testing.

SUMMARY

Activity in this program was directed to an analysis of the technical and economic aspects of emission controls in the paint and varnish manufacturing industry. The main objective of the study was to provide an improved technical and economic basis which the Environmental Protection Agency could use to evaluate emissions and control technology in the paint and varnish industry. Industry structure and statistics, the nature and sources of emissions, technical problems associated with emission controls, cost of emission control equipment and the overall economic impact of air pollution control were among the major topics investigated in the program. The salient results of the program are highlighted in the following sections.

Process and Emissions

Significant air pollution problems associated with this industry are localized odor nuisance complaints and fugitive solvent vapors. The odor complaints result primarily from open kettles, varnish cooks, closed reactor resin cooks and handling operations of low odor threshold raw materials. The quantity of this type of emission is very small but, nevertheless, contains a wide variety of highly odorous substances. Fugitive and non-fugitive solvent losses represent the major quantity of emissions from the manufacturing operations but these amount to only a small percent of the solvent losses which occur during the application and drying of coatings.

A brief history and description of the paint and varnish industry is presented in this chapter. The various production processes and manufacturing steps are discussed. The chemistry of varnishes and resin cooking is presented in some detail with the production of alkyd resins given major emphasis. Other resins discussed are vinyl, acrylic, epoxy, urethane, cellulosic, amino, hydrocarbon, phenolic and silicone.

Process information gathered from an industry questionnaire is summarized. A total of 452 questionnaires were mailed to 382 different paint companies. Of these, 338 or about 75 percent were used in the process information summaries presented. Included in these summaries is a listing of major products, raw materials and production equipment.

The design basis and material balance of the model plant developed to evaluate the economics of the industry are presented in detail. The design of the plant was based on a study made by the Management Committee of the National Paint and Coating Association and presented at the 1972 NPCA annual meeting in a paper by Mr. R. F. Brewster. The model plant was modified in capacity to more closely approach the average size plant reported in the industry questionnaire. On-site resin production facilities were also added.

A description of the type, source and quantity of emissions that are encountered in the production of paints and varnishes is discussed along with the influence of various process operations on these emissions. Emission data from the industry questionnaire, source tests by afterburner equipment manufacturers and source tests conducted by the Federal EPA are summarized and presented. Primary emphasis was placed on emissions from varnish and resin cooking. A detailed source by source calculation of emissions from the model plant is also presented. Finally, there is a brief discussion of liquid and solid wastes.

Primary sources of gaseous emissions are: varnish cooking, resin cooking and thinning. Secondary sources of gaseous emissions are: handling and storage, milling operations, blending and finishing, and filling. The primary source of particulate emissions is the pigment dusting encountered in the milling operation.

As a part of this study, the Federal EPA conducted 10 source tests on emissions from the production of four types of resins in four different resin reactors. The work was carried out by Scott Research Laboratories under the direction of the EPA source test group. Flow rates, total hydrocarbons and gas chromatography data were obtained and are summarized and presented.

Industry Statistics

The Paint and Allied Product Industry (SIC 2851) is made up of approximately 1,727 establishments operated by some 1,365 companies. In this chapter, the type, size and geographical distribution of these plants are presented and analyzed. Past, present and projected industry trends to the year 1985 are also presented and discussed. Data is presented on production and production capacity relations, number of plants, size of plants, and typical plant and equipment ages. A discussion of the influence on the future of this industry due to technical innovation and other outside effects is also presented.

Measurements of Emissions

As yet, there is no tried and proven method for source measurements of hydrocarbons. This problem is even further complicated by the large variety and highly cyclic nature of the emissions emitted from paint and varnish kettles. In this chapter, these problems and the current state-of-the-art for both source and continuous monitoring are discussed. Detailed descriptions of the methods currently used by industry and regulatory agencies are discussed. A description of the method used by the Federal EPA during the source testing conducted for this study is also presented.

Inventory of Emissions

In this chapter, emission factors are developed for this industry as a function of production capacity and type of product. Solvent emission factors were developed for three types of plants.

Plants Producing Resins Only	13,700 lb/MM lb Resin
Plants Producing Resins & Paints	45,000 lb/MM gal Solvent Based Paint, 5,460 lb/MM lb Resin
Plants Producing Paints Only	56,000 lb/MM gal Solvent Based Paint

Data collected from the industry questionnaire was used as the basis for the above emission factors. The emission factors for plants producing both paint and resins compare well in total with those calculated for the study's model plant. As might be expected, these emission factors represent averages of widely differing individual plant emissions and care should be exercised in applying them arbitrarily to specific plants.

By using an average gaseous emission factor of 50,000 pounds per million gallons of solvent based paint produced and paint production for 1972, potential gaseous emissions in the U.S.A. from paint production are estimated to be 17,900 tons for the year 1972. A geographical distribution of organic emissions is presented in Figure 41 on page 198.

Emission Control Technology

In this chapter, a detailed discussion of the existing state-of-the-art of air pollution control for the paint and varnish industry is presented. The discussion includes a description of the best control techniques for each emission source, alternate control techniques, methods of control other than add-on equipment, performance of currently used systems and capability of best control systems to meet more stringent standards. Potential water and solid waste disposal systems are also reviewed. Best control for pigment particulate emissions are fabric filters. Best control for gaseous emissions including odors are catalytic and thermal afterburners. Considerable discussion is devoted to the design and application of afterburner systems to resin and varnish kettles. A discussion of the use of a refrigerated condenser as an alternate control device is also included.

Inspection Procedures

This section of the report was written for enforcement officers to assist them when entering and inspecting paint, varnish and resin facilities and details the type and location of emission problems and control equipment. It was written to provide the compliance inspector with an understanding of the industry sufficient to conduct a proper inspection.

Economics of Emission Control

Specific among the goals of this study was the determination of the financial impact of air pollution control on the paint and coating industry. To accomplish this, the investigation was divided into the three following parts:

Cost of Best Control Equipment
Model Plant Economic Study
Projections of Present and Future Industry-wide Costs

Costs of best control equipment were obtained from equipment manufacturers through the Industrial Gas Cleaning Institute which was retained as a subcontractor. These were obtained in response to detailed process, operating and bid specifications prepared by Air Resources, Inc. This information was then summarized and is graphically presented within this section. The capital cost and total annual operating cost for turnkey systems, catalytic and thermal afterburners plus auxiliaries and afterburners only are presented. These costs are plotted against size as measured by gas flow. Separate plots are presented for afterburners with and without heat exchange.

Model plant costs were developed by the Sherwin-Williams Company who acted as a subcontractor for this specific purpose. A detailed capital cost of the model plant was made by their engineering department. Balance sheets and operating statements for both the controlled and uncontrolled plants were developed by their accounting department. Present total cost and fifteen-year projected cost of the use of best control by the industry were also developed and are summarized below:

Total Cost to Industry for Best Control

Capital Investment Cost	$16,200,000
Annual Operating Cost	4,500,000

Projected Cost of Control (15-year period)	
Capital Investment Cost	$30,600,000
Annual Operating Cost	8,500,000

The application of best control technology to the model plant will result in a loss of income ranging between $0.006 and $0.008 per gallon of paint produced. This is equivalent to a decrease in stockholder equity of between 1.73 and 3.25 per cent.

Please note that all costs presented in this chapter are based on 1972 monetary values and do not provide escalation factors for current requirements.

Pigment Industry

For purposes of this study, the pigment industry was included as part of the paint and varnish industry. General statistics for the industry are presented followed by a review of the pigments judged to have the most potential for significant air pollution emissions. Major pigments studied were the cadmium pigments, zinc oxide, the chrome pigments, iron oxide and titanium dioxide. Of these, the manufacture of titanium dioxide by both the sulfate process and the chloride process was studied in further detail. A study of emission control technology was also conducted and includes type and performance of currently used emission control systems and other potential methods of control.

An industry questionnaire similar in content to the paint and varnish questionnaire was prepared specifically for the titanium dioxide manufacturers. The results of the questionnaire are summarized and presented. Estimated emission factors for various operations utilized by both the sulfate and chloride process were developed and are also presented.

Recommended Research and Development Programs

The deficiencies in both pollution control technology and emission measurements are treated in detail and recommendations are made for research and development programs which can lead to improvements in these areas.

Recommended programs for improvement in air pollution control technology are as follows:

1. Design of a closed reactor for resin and varnish cooking.
2. Development of liquid handling of resin cook raw materials.
3. Development of inexpensive solvent scavenging system.
4. Development of transfer system for direct flame incinerator.

5. Determination of best existing control technology currently applied to the manufacture of TiO_2 by the sulfate process.

Recommended program for improvement in emission measurements is as follows:

1. Development of a simple and inexpensive instrument to detect hydrocarbon emission and measure flow from kettle cooking operations.

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CHAPTER 1

PROCESS AND EMISSION

In this chapter a discussion of the process operations used in the manufacture of paint, varnishes and resins will be presented. The type, quantity and source of emissions evolved from these processes will also be presented.

I. PROCESS

This section will cover process operations only. The discussion will include a brief history of the industry, a description of the various manufacturing processes, the influence of process operation on emissions and detailed material balances. The material balance will be based on the model plant developed for the industry.

A. Detailed Process Description

1. History — The paint and varnish industry is one of the oldest manufacturing industries in the United States. The industry is made up of about 1,500 companies operating about 1,700 plants.[1] The industry is well distributed geographically throughout the country and production volume is definitely related to density of population. Even though about 36 companies account for about 64% of the total sales, the industry is one of the few remaining which contains numerous small companies that specialize in a limited product line to be marketed within a geographical region. There are fewer than 20 companies that sell paint nationwide.

The industry is now emerging as a scientific business from its beginning as an art, 50 years ago. Even with rapid growth in technology, the industry process techniques still are not well defined and not only vary from one producer to another but there is also variation in the techniques used by a single producer. To add further complication, the industry is technically one of the most complex of the chemical industry. A plant that produces a broad line of products might utilize over 600 different raw materials and purchased intermediates. These materials can be generally classified in the following categories: oils, metallic driers, resins, pigments, extenders, plasticizers, solvents, dyes, bleaching agents, organic monomers for resins, and additives of many kinds.

The industry produces an equally large number of finished products which are generally classified as trade sale finishes, maintenance finishes, and industrial finishes.

Trade sale products are stock-type paints generally distributed through wholesale-retail channels and packaged in sizes ranging from 1/2 pint to 1 gallon. A subdivision of trade sale products are maintenance finishes which are used for the protection and upkeep of factories, buildings, and structures such as bridges and storage tanks. Since they are usually stock type, they come under the Department of Commerce definition of trade sales.

The other major type of paint products are industrial finishes which are generally defined as those applied to manufactured products. These finishes, such as automotive, aircraft, furniture, and electrical finishes are usually specifically formulated for the using industry. Within these major product lines there are literally thousands of different products for many different applications and types of customers. Trade sale finishes and industrial finishes are produced in almost equal volume with the production for 1972 estimated at 465 million gallons for trade sales and 485 million gallons for industrial finishes. Trade sales, however, are estimated to account for 55% of the dollar sales or about $1,715 million dollars.[1]

2. Description of Manufacturing Process — Starting with all purchased raw material, the manufacturing process for pigmented products appears simple from a schematic viewpoint. Basically, it consists of mixing or dispersing pigment and vehicle to give the final product. This process is schematically illustrated in Figure 1.

The paint vehicle is defined as the liquid portion of the paint and consists of volatile solvent or dispersing medium and non-volatile binder such as oils and resins. The non-volatile portion is also called the vehicle solid or film former. The pigment portion of the paint consists of hiding pigments such as titanium dioxide (TiO_2), extenders such as talc or barium sulfate, colorants, and any mineral matter used for flatting or other purposes.

Also included in the non-volatile portion of the coatings are various additives present in small quantities for a variety of reasons. From an environmental standpoint the most important of these are the preservatives and the driers. The preservatives are fungicides and mildewcides which sometimes contain mercury compounds. While they are present in small quantities, they have nevertheless become of interest to health and regulatory agencies. It is anticipated that the use of mercury will be substantially eliminated in the next few years.

The driers are catalysts whose purpose is to promote the oxidative cross-linking of the resins and/or oils used in coatings. Without such catalysts many of the coatings in use today would not be

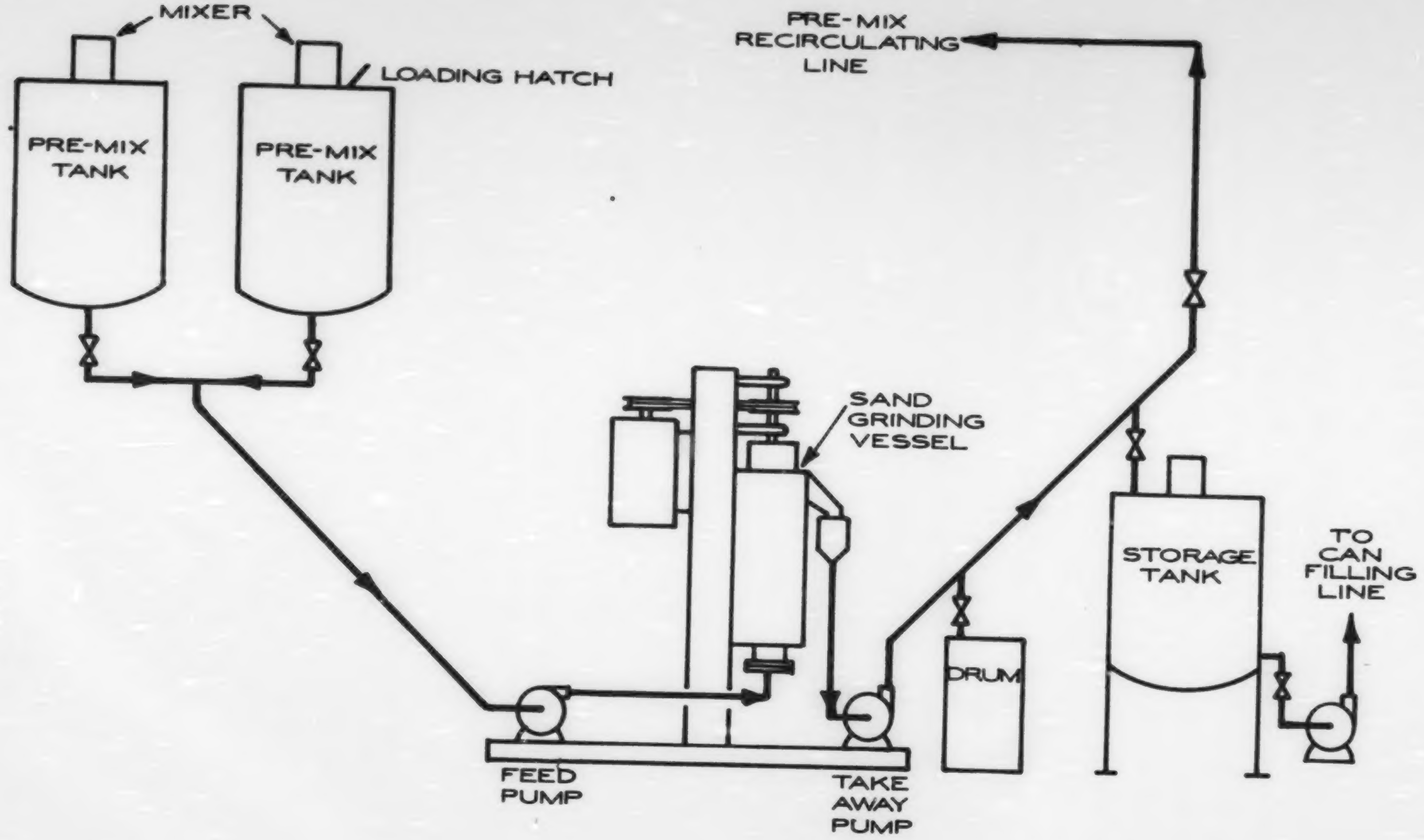


FIGURE 1

PAINT MANUFACTURING USING SAND MILL FOR GRINDING OPERATION possible since they would never dry completely, or at least would dry too slowly to be of practical value. The common driers are organic acid salts of lead, cobalt, calcium, zinc, manganese, or zirconium. Lead naphthenates have historically been the most often used but recent regulations limiting lead to 0.5% of the dried film and possibly more stringent future regulations have prompted some degree of reformulation of the drier systems.

The incorporation of the pigment in the paint vehicle is accomplished by a combination of grinding and dispersion or dispersion alone. When it is necessary to further grind the raw pigment, pebble or steel ball mills are normally used. With the advent of fine particle grades of pigment and extenders, as well as the wide spread use of wetting agents, the trend is toward milling methods that are based on dispersion without grinding. Dispersion consists of breaking up of the pigment clusters and agglomerates, followed by wetting of the individual particles with the binder or vehicle. Some of the more popular methods currently being used are high-speed disc impellers, high speed impingement mills and the sand mill.

Some typical paint formulas, both simple and complex, are listed below and on the following page.

WHITE ACRYLIC BAKING ENAMEL*

	lb	gal
Rutile TiO_2	220.3	6.64
Thermosetting acrylic resins (50% NVM)	444.1	54.20
Melamine resin (100% NVM)	95.2	9.52
Catalyst for melamine	6.63	0.87
Xylol	184.0	25.51
Ethylene glycol monoethyl ether acetate	26.4	3.26
	976.3	100.00

---

*Formulas courtesy of Ashland Chemical Company.

WHITE GLOSS INTERIOR ENAMEL*

	lb	gal
Rutile TiO_2	300.0	9.02
Suspension and flow agent	8.0	1.15
Long-oil, tall oil alkyd (70% NVM)	536.0	67.0
Mineral spirits	150.0	23.08
6% Co naphthenate	4.4	0.56
4% Ca naphthenate	9.4	1.25
6% Zr drier catalyst	12.5	1.75
Antiskinning agent	1.0	0.13
	1,021.3	103.94

POLYVINYL ACETATE EMULSION WALL PAINT*

Grind (high speed mill)	lb	gal
Water	275.0	33.05
KTPP, dispersant	2.0	0.10
R&R-551 soya lecithin dispersant	8.0	0.92
Tergitol® NPX, dispersant	2.0	0.23
Nopco® NDW, anti-foamer	0.5	0.07
Rutile titanium dioxide	200.0	5.94
Diatomaceous silica	45.0	2.34
Clay	130.0	6.05
Calcium carbonate	100.0	4.43
Sub-total	762.5	53.13
Reduction		
Methocel® 65HG (3½% solution)	120.0	14.42
Carbitol® acetate, coalescing agent	25.0	2.98
Nopco® NDW, anti-foamer	0.5	0.07
PVAc emulsion	224.0	24.62
Water	10.0	1.20
Pre-mix		
PMS-30, mildewcide	0.3	—
Water	30.0	3.61
Total	1,172.3	100.03

---

*Formulas courtesy of Ashland Chemical Company.

Aside from the dispersion step, pigment paint manufacturing involves handling of raw material as well as handling and packaging of finished product.

Air pollutant emissions are primarily the fugitive type and consist of evaporation losses of the volatile portion of the vehicle from the milling operation and from various product holding tanks and packing stations. There are also some fugitive particulate emissions that result from handling and emptying of pigment or extender bags into the grinding and dispersion mills. In some plants these loading areas are hooded and bags and pigment dusts are passed to a central collection station. At this station bags are removed for refuse disposal and the pigment dust is collected in a fabric filter and recycled into primer or other dark paint mixes.

Some of the larger and a few of the medium manufacturers make a significant amount of their formulation ingredients, such as pigments, resins, and modified oils. Some manufacturers produce these ingredients in an amount exceeding their requirements and sell the excess to other manufacturers. A significant number also make only a portion of their resins and purchase the remainder from their competitors or suppliers who specialize in resin manufacturing.

The manufacturing of resins and varnishes is by far the most complex process in a paint plant, primarily as the result of the large variety of different raw materials, products and cooking formulas utilized. One manufacturer has reported that he has over 9,300 active resin formulas. Of these 600 to 700 are in general monthly use while the remainder are produced on an intermittent basis. Furthermore, new formulas are added at the rate of 5 to 10 per month. While this plant is not typical since it produces a more diverse product line than most, it nonetheless serves to illustrate the wide diversity found in the industry. This diversity is the source of the difficulty that is encountered in attempting to characterize the industry or in making generalized statements about emissions, control technology, or any other subject for that matter.

The complexity begins with the nomenclature used in classification of the final product. Originally, varnishes were all made from naturally occurring material and they were easily defined as a homogeneous solution of drying oils and resins in organic solvents. As new synthetic resins were developed, the resulting binders or varnishes were classified on the basis of the resins used. Examples of this are alkyd, epoxy, and polyurethane resins. In an attempt to simplify nomenclature the industry is attempting to adopt the term "clear coating" to cover some varnishes, resins and lacquers.

There are two basic types of varnishes, spirit varnishes and oleoresinous varnishes.[2] Spirit varnishes are formed by dissolving a resin in a solvent and they dry by evaporation of the solvent.

The dry film formed undergoes no substantial change in the process of drying and is classified as non-convertible. A good example of this type of varnish is shellac which is a mixture of a natural resin and alcohol.

Materials that might fall in the general category of spirit varnishes, that use nitro-cellulose or similar compounds for their basic film former, have by common practice been termed lacquer. These are defined as a colloidal dispersion or solutions of nitro-cellulose, or of similar film-forming compounds, with resins and plasticizers in solvents and diluents which dry primarily by solvent evaporation. One of the advantages and general characteristics of spirit varnishes is that upon recoating, the film will soften and partially redissolve so that patched areas show no sharp line of demarcation.

Oleoresinous varnishes, as the name implies, are solutions of both oils and resins. These varnishes dry by solvent evaporation and by reaction of the non-volatile liquid portion with oxygen in the air to form a solid film. They are classified as oxygen convertible varnishes and the film formed on drying is insoluble in the original solvent. A summary of the various types of material used in the production of classical oleoresinous varnishes is given in Table 1.

Varnish is cooked in both portable kettles and large reactors. Kettles are used only to a limited extent and primarily by the smaller manufacturers. The very old, coke fired, 30 gallon capacity copper kettles are no longer used. The varnish kettles which are used, have capacities of 150 to 375 gallons. These are fabricated of stainless steel, have straight sides and are equipped with three or four-wheel trucks. Heating is done with natural gas or fuel oil for better temperature control. The kettles are fitted with retractable hoods and exhaust pipes, some of which may incorporate solvent condensers. Cooling and thinning is normally done in special rooms. A typical varnish production operation is illustrated in Figure 2.

All of the resin manufacturers and most of the large and medium size paint manufacturers utilize large indirectly heated closed reactors for varnish production. These reactors will be described in more detail in later report sections covering modern resin manufacturing.

The manufacturing of oleoresinous varnishes is somewhat more complex than for spirit varnishes. Manufacture of this product consists of the heating or cooking of oil and resins together for the purpose of obtaining compatability of resin and oil and solubility of the mixture in solvent as well as for development of higher molecular weight molecules or polymers.

The time and temperature of the cook are the operating variables used to develop the desired end product polymerization or "body". The chemical reactions that occur are not well defined. The resin is a polymer before cooking and may or may not increase in molecular size during the cook.

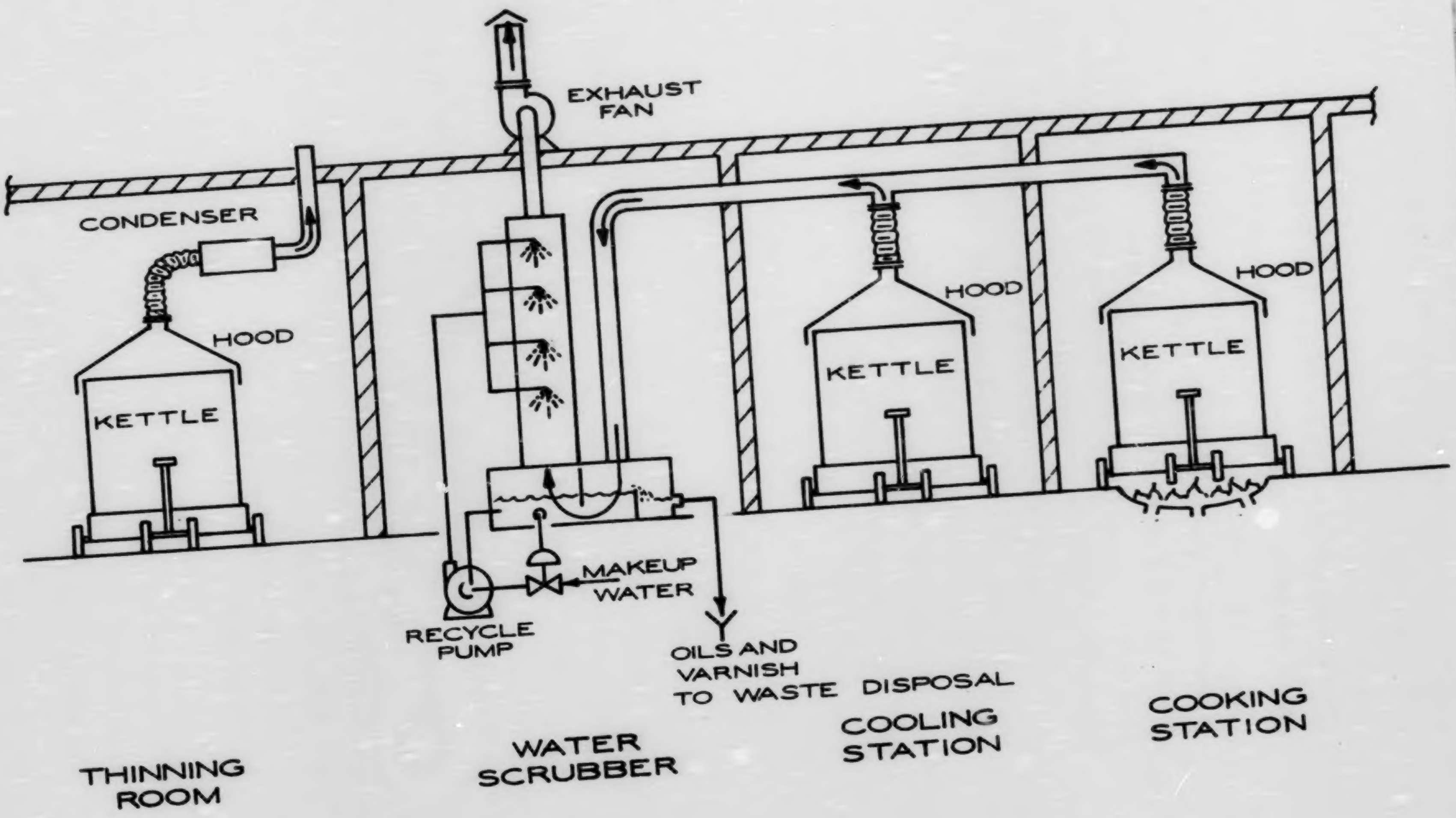
TABLE 1

VARNISH RAW MATERIALS[2]

Oils	Resins	Solvents	Driers	Additives
1. Hard	1. Natural	1. Mineral Spirits	1. Lead	1. Anti-Skinning agents
a. Tung	a. Fossil resin, congo	2. VM&P Naphtha	2. Manganese	2. Ultra-violet absorber
b. Oiticica	kauri, pontianak	3. Toluol	3. Cobalt	3. Flattening agents
c. Dehydrated castor oil	b. Semi-fossil resin	4. Xylol	4. Calcium	
2. Soft	manila, boea, batu,	5. Terpene solvents	5. Zirconium	
a. Linseed	eastindia			
b. Safflower	c. Recent and crop resin			
c. Soya	dammar, accroides			
d. Fish	sandaral mastic, elemi,			
e. Tall oil fatty acids	shellac			
3. Chemically modified	d. Rosin, gum rosin,			
a. Maleic-treatment	wood rosin, tall oil			
	rosin, rosin esters			
	2. Synthetic Resin			
	a. Maleic resin, phenolic resin			
	3. Metallic Soaps			
	a. Limed rosin			
	b. Zinc resinate			

FIGURE 2

TYPICAL VARNISH COOKING ROOM



The resin may react with the oil to produce copolymers of oil and resin, or it may exist as a homogeneous mixture or solution of oil homopolymers and resin homopolymers.

In special cases it is possible to produce oleoresinous varnish without the application of heat by simply dissolving or "cold cutting" the resin and heat bodied oil in the solvent. Heat bodying or polymerization of an oil is done to increase its viscosity and is carried out in a kettle in a fashion similar to varnish cooking. The fundamental reaction that occurs is polymerization of the oil monomers to form dimers with a small portion of trimers.

It is possible to blend resins and heat bodied oil and obtain the same varnish that can be produced by cooking the resin and the unbodied oils. This indicates that copolymerization is not the fundamental reaction in varnish cooking.

A fundamental variable that determines the final property of a varnish is the proportion of oil to resin. It is expressed as gallons of oil to 100 pounds of resin. On this basis, varnish is generally classified as follows:

Short oil:	5 to 15 gallons (28 to 54% oil*)
Medium oil:	16 to 30 gallons (54 to 70% oil*)
Long oil:	30 to 60 gallons (70 to 86% oil*)

*Percentages based on an oil of approximately 7.8 lb/gal.

A myriad of formulations are used in varnish manufacture. Typical varnish cooking formulations are given below:[2]

20 GALLON CAN COATING VARNISH — STRAIGHT COOK

	lb	gal
Amberol M-88 modified phenolic resin*	100	11.24
Castung® 403 Z_3 dehydrated castor oil**	160	20.00
Kadox® 25, ultra-fine zinc oxide***	3	—
Manganese naphthenate (6% Mn)	2	0.25
Mineral spirits	235	36.70
Theoretical yield	500	68.19

* Rohm and Haas Co.

** Baker Castor Oil Co.

*** New Jersey Zinc Co.

Procedure

Heat resin and oil to 580°F (304°C) in 45 minutes. Add zinc oxide and hold 580°F about 30 minutes to body (50 seconds Ford No. 4 Cup at 52% solids in mineral spirits). Cool quickly by water spray to 450°F (232°C) add thinner and drier and filter carefully.

Constants

Solids	52% minimum
Viscosity	50 to 60 sec. in Ford No. 4 Cup (about G-I)
Color, Gardner 1933	14 to 18
wt/gal	7.4 lb

The above formula is made in portable kettles. High temperature is necessary to develop maximum resistance, yet cooling must be fast to avoid overpolymerization. It is probably impossible to handle batches larger than 300 gallons safely.

PHENOLIC RESIN SPAR VARNISH* — DISPERSION METHOD

	lb	gal
Phenolic resin CKM 5254	100.0	10.0
Alkali refined linseed oil	85.0	11.0
Tung oil	164.0	21.0
Refined castor oil	8.0	1.0
Mineral spirits	202.0	31.0
Dipentene	26.9	3.8
Turpentine	26.9	3.8
n-Butyl alcohol	13.45	2.0
Theoretical yield	626.25	83.6

Procedure

Heat the resin and linseed oil to 560°F (293°C) for 30 minutes for body. Check with tung oil. (Reduces to about 350°F.) Reheat to 450°F (232°C) in 15 minutes for body, add castor oil, thin and filter.

Properties

Viscosity	C to D
Solids	57%
Color, Gardner 1933	11
wt/gal	7.57 lb

---

*Formula courtesy of Union Carbide Corporation, Chemicals and Plastics

Driers (on oil)

Lead	0.1%
Cobalt	0.01%
Manganese	0.005%

INSITU GENERAL PURPOSE VARNISH — UNIPHASE METHOD[2]

	lb	gal
Alkali refined soya oil		23.7
Hydrated lime paste*	grams 32	
Pentaerythritol	19	
Glycerol	21	
Tall oil rosin	135	
Maleic anhydride	38	
Mineral spirits	372	58.0
Activ 8**	fl oz 2	
Calculated net yield, allowing for loss in processing		100.0

Procedure

Maintain CO_2 over batch throughout the cook. Heat soya oil to 400°F (204°C), add lime paste, gain 450°F (232°C). Add the pentaerythritol slowly, keeping the temperature at 425 to 450°F for 45 minutes. Open condenser, close stack, and heat to 470°F (243°C). Hold at 460 to 470°F. Add the glycerol through the funnel, keeping the temperature above 425°F. Heat to 460°F, and hold 460 to 470°F for solubility of at least 2:1 in methanol. Cool to 400°F by circulating cold Dowtherm through the jacket. Open stack and close the condenser. Add the rosin. After the rosin has melted, add the maleic anhydride. Heat to 520°F and hold for a reduced viscosity of I-J at 50% solids in mineral spirits. Drop to 480°F (249°C) and hold for a reduced viscosity of T-U. Cool, thin and filter.

The major problem in varnish cooking is control of cooking time and temperature to yield the desired product and prevention of over bodying or gelation. This is done by a variety of cooking methods and control techniques. The main methods for cooking modern oleoresinous varnishes are listed below and the technique used is primarily a function of the type of ingredients employed.

---

* Hydrolysis catalyst, a paste of hydrated lime in soya oil.

** An organic drying catalyst — R. T. Vanderbilt Co. It supplements metallic driers; does not replace them.

1. Regular or straight cook.
2. Oil-checked method.
3. Resin-checked method.
4. Dispersion method of split-cook.
5. Insitu or uniphase method.

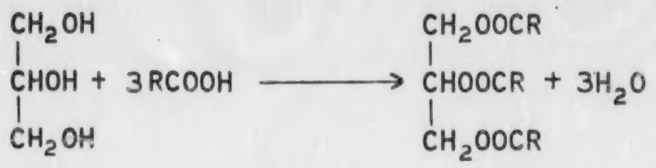
These various methods are used to prevent gelation and/or improper dispersion. Methods (1) and (4) apply when cooking varnishes from the material listed in Table 1. They are suitable for cooking in the small portable kettles discussed earlier. Control of these cooks is done by examination of a cold pill on glass. The criteria used are the clarity and the tack and string of the pill when touched.

The fifth method, listed above, for insitu cooking is carried out primarily in large set kettles or reactors. As indicated in the insitu formula listed earlier, the principle of this type of cooking is simultaneous reaction of basic raw material to form resin or both resin and oil which further react to form the desired varnish in one continuous operation. This is a much more complicated cook and more sophisticated control is required. The end point of the cook is controlled by periodic viscosity measurements or using a remote viscosity instrument. The reaction is carried out in a closed kettle blanketed with an inert atmosphere. An inert gas is bubbled through the mixture to aid in the removal of water formed from esterification of the organic and/or rosin acids and polyols. The reactions involved are illustrated on the following page.

Resins, along with drying oils, make up the backbone of surface coatings since they are responsible for the formation of a film with physical integrity and adhesion. It is the ability to form this film that differentiates paint from a mere mixture of pigment and vehicle. Film formers are such a critical component of the finish product that the latter is generally classified by the predominant resin associated with it (e.g. epoxy and polyurethane).

In their original usage resins were various natural solid and semi-solid organic substances (such as rosin and shellac) exuded from certain plants and trees, however, since the mid 1920's natural resins have been supplanted by synthetically manufactured chemicals. Manufactured phenolics first became commercially available in 1924, alkyd vehicles in 1925, and alkyd resins modified by urea-formaldehyde in 1925. Each of these introductions represented a major breakthrough in the

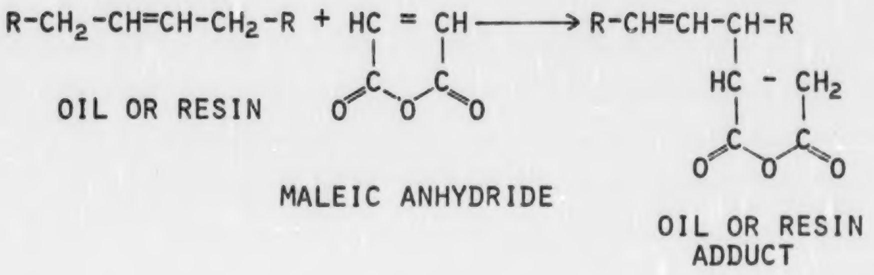
FATTY ACID TO OIL

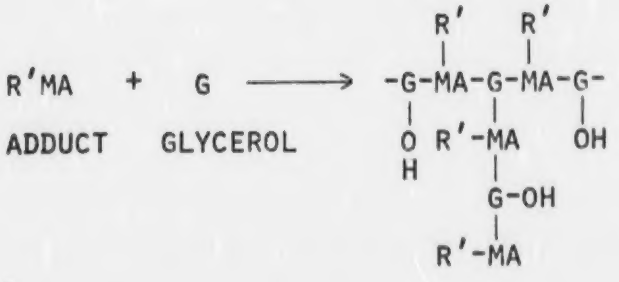


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOOH \longrightarrow \begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2OOCR \end{array} + 3H_2O$$

Plyol (Glycerol) + 3 Fatty Acid → Triglyceride + 3 water

MALEIC RESIN





MALEIC RESIN

production and application of surface coatings. In 1970 resins accounted for approximately 18% by weight and 40% by production value of all chemical raw materials consumed by the paint and varnish industry (this was equivalent to about $0.32/lb for synthetic resins as opposed to $0.15/lb for total raw materials). By comparison natural resins comprised less than 2% of total film formers in 1970 where prior to World War II they had contributed more than 50%.[3]

There is a large variety of synthetic resins produced for use in the manufacture of surface coatings. A listing of the more popular resins is given below. They are listed by order of 1970 consumption by the coatings industry.[3]

Resin	Consumption — 1970 (million pounds)
Alkyd	680
Vinyl	300
Acrylic	220
Epoxy	80
Cellulosic	65
Amino	60
Urethane	55
Rosin ester	50
Styrene	40
Phenolic	35
Hydrocarbon	30
Other synthetic	45

By far the most widely used resins are the alkyds whose consumption is twice that of its nearest rival, the vinyls. Oil free polyesters, included in the "other" group in 1970, are enjoying rapid growth. Based on the questionnaire sample obtained for this study, 1972 production was at least 91 million pounds.

Resins are polymer molecules built up from simpler units, or building blocks. The union of these building blocks is generally brought about by the action of heat and catalyst. When the polymer molecule is a simple repetition of the same unit it is a homopolymer; when two or more different type units are present a copolymer results. To be capable of polymerizing, a monomer must contain chemical groups that have potential chemical reactivity. The major monomers used are those containing one ethylene double bond which permits very long chain polymers.

There are two types of polymers used in coatings: condensation polymers and addition polymers. A condensation polymer is a polymer formed from the reaction of two (or more) different types of molecules with the splitting out of some product, usually water. Addition polymers are formed from the "addition" of molecules, or monomers, to form the larger molecule without any other reaction product.

Examples of condensation polymers include polyesters, amino resins, and alkyds. Alkyds are really oil modified polyesters and constitute the most important groups. Polyester type resins are formed from acid-alcohol reactions. Polymer formation requires the use of polyfunctional reactants. Difunctional reactants produce linear polymers while the use of trifunctional, or higher, constituents permits branching and cross linking to take place.

Examples of addition polymers include the acrylics and vinyls. These proceed via a free radical mechanism in the presence of a catalyst to produce linear polymers. Modifiers can be introduced to produce cross linking where desired.

In addition to the kind of building blocks used, the average number units in (or total molecular weight of) the product molecule determines properties of the resin. In general, increasing molecular weight improves film hardness, strength, resistance to water, chemicals and solvents but also results in reduced solubility and higher viscosity. Of course, ultimate film properties can also be determined by appropriate combinations of two, or more, resin types. In fact, a significant portion of coating formulations utilize such combinations.

Alkyd Resin — Alkyds are widely used for a variety of reasons. They are ideal vehicles for pigmented coatings and exhibit good wetting and dispersing properties. They use low cost solvents with minimum odor and produce coatings having excellent durability, flexibility and gloss retention. Coatings can be formulated with good solvent resistance, toughness, heat resistance, and color retention.

Alkyds can be combined with any of the following materials.[5]

Nitrocellulose
Urea-formaldehyde resins
Melamine-formaldehyde resins
Phenolic resins
Ethyl cellulose
Chlorinated rubber
Chlorinated paraffin
Epoxy resins
Polyisocyanates
Silicone resins
Polyamides
Natural resins
Cellulose acetatebutyrate
Monomers (styrene, vinyl toluene, methyl methacrylate)
Synthetic latices (styrene-butadiene,
  polyvinyl acetate, acrylic)

Alkyd resins comprise a group of synthetic resins which can be described as oil-modified polyester resins. They are produced from the reaction of polyols or polyhydric alcohols, polybasic acids and oils or fatty monobasic acids. A listing of commonly used raw material is given below:

Oils or fatty acids[2]

Linseed
Soybean
Safflower
Tall oil fatty acid
Tall oil
Fish
Tung (minor)
Oiticica (minor)
Dehydrated castor (minor)

Castor
Coconut
Cottonseed
Lauric acid
Pelargonic acid
Isodecanoic acid
Isooctanoic acid

The materials in the first column are oxidizing or drying types. The materials in the second column are non-oxidizing and yield soft non-drying alkyds which are used primarily as plasticizers with hard resins. The acids shown in the last column are the only materials that are strictly synthetic in origin.

Oils or fatty acids impart flexibility and drying to an alkyd. In general, the greater the unsaturation (measured by iodine value), the greater the drying or hardening properties. The use and characteristics of these oils was discussed earlier under varnish manufacturing.

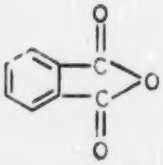
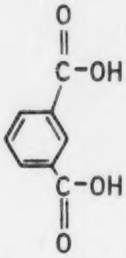
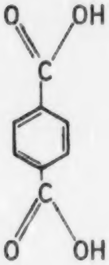
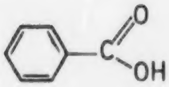
Glycerol or glycerine was the first polyol used for alkyds. This material was first obtained as a byproduct of the splitting of fat and oils in soap manufacturing. Also, glycerine is now produced synthetically from petroleum sources and is supplied at a purity of 99+%. Glycerine has historically been the most widely used polyol for alkyds.

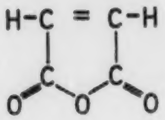
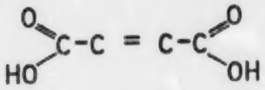
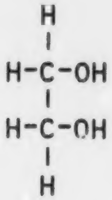
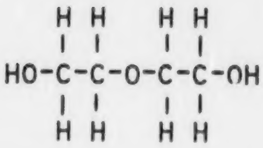
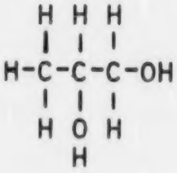
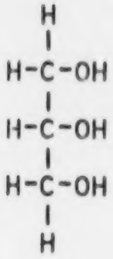
At the present time, however, the leading polyol, based on usage, is pentaerythritol (PE), which came into common use in the 1940's. PE is supplied as "technical grade" material and contains mono, di, tri and polypentaerythritol. The material consists primarily of the mono form which is illustrated on page 20.

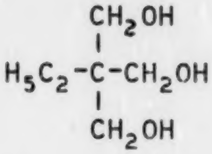
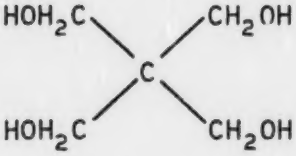
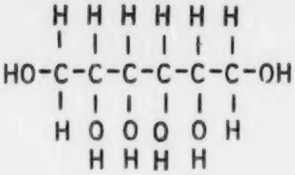
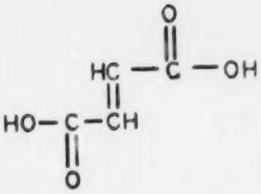
The choice of which polyol to use is based on both technical and economic factors. For some applications glycerine based alkyds are more suitable, while for others, pentaerythritol is better. In many cases, however, a suitable alkyd can be formulated from either and for these a choice can be made on the basis of cost or availability. Present economics favor pentaerythritol.

The important distinguishing feature of the various polyols is the number of potentially reactive hydroxyl groups in the molecule, known as functionality. The glycols with a functionality of two produce only straight chain polymers and their alkyd resins are soft and flexible. The resultant products are used primarily as plasticizers for hard resins. They are the least expensive polyols and are blended with more reactive polyols such as PE. Glycerine has a functionality of three and is used primarily in short and medium oil alkyds. Pentaerythritol, with a functionality of four, cross links to a greater extent, forming harder polymers. It is ideal for use in long oil alkyds. However, due to its high reactivity, it presents problems of end point control in processing of short or medium oil alkyds. Dilution with ethylene glycol, as discussed earlier, reduces this latter problem and increases solubility in the oils.

Acids and Anhydrides

Name	Formula	Form
Phthalic anhydride (ortho)		White solid
Isophthalic acid (meta)		White needles
Terephthalic acid (para)		White crystals
Benzoic acid		White solid

Name	Formula	Form
Maleic anhydride		White solid
Maleic acid		White solid
Ethylene glycol	 $\begin{array}{c} H \\ \vert \\ H-C-OH \\ \vert \\ H-C-OH \\ \vert \\ H \end{array}$	Liquid
Diethylene glycol	 $\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & \vert & & \vert & & \vert & & \vert & \\ HO- & C & - & C & -O- & C & - & C & -OH \\ & \vert & & \vert & & \vert & & \vert & \\ & H & & H & & H & & H & \end{array}$	Liquid
Propylene glycol	 $\begin{array}{ccccccc} & H & & H & & H & \\ & \vert & & \vert & & \vert & \\ H- & C & - & C & - & C & -OH \\ & \vert & & \vert & & \vert & \\ & H & & O & & H & \\ & & & H & & & \end{array}$	Liquid
Glycerine CP-95% glycerine Super-98%	 $\begin{array}{c} H \\ \vert \\ H-C-OH \\ \vert \\ H-C-OH \\ \vert \\ H-C-OH \\ \vert \\ H \end{array}$	Liquid

Name	Formula	Form
Trimethylolepropane	 $H_5C_2-C(CH_2OH)_2-CH_2OH$	White solid
Pentaerythritol		White solid
Sorbitol	 $HO-CH_2-(CHOH)_4-CH_2-OH$	White solid
Fumaric acid		White solid

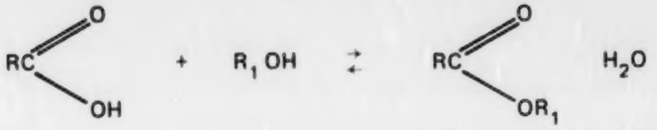
The acidic material may be used in the form of an acid or an anhydride. An acid anhydride is formed from the elimination of one molecule of water from two carboxylic acid groups and is preferred since it reacts faster and yields less water to be removed from the cook.

For many years, phthalic anhydride (ortho) was the only polybasic acid used in substantial proportions in alkyds. It still remains the predominant dibasic acid. PA is produced from the catalytic oxidation of naphthalene or ortho-xylene. Some resin manufacturers produce their own PA. However, this process will not be studied here since it is more properly part of the petrochemical industry.

Some of the acids listed above, such as benzoic acid, are monobasic or monofunctional, and cannot be used as the sole organic acid. They are used to terminate alkyd polymers and to modify the properties of resins. Benzoic acid is substituted for part of the fatty acids. It makes the resin harder and less flexible as well as enhancing the gloss.

The chemistry of alkyd resin systems is very complex. So much so that theoretical considerations offer only a good starting point. Final formulae and variations are developed by trial and error changes, based on performance requirements and shortcomings of previous batches.

Condensation is the reaction basic to all polyester resins, including alkyds. This reaction follows the elementary equation for esterification as shown below:



Acid + Alcohol $\rightleftarrows$ Ester

For Alkyd Resins

PA + Glycerine $\rightleftarrows$ Glycerol phthalate + H_2O

The ester monomer formed is very complex and further reacts to form large polymers called resins. The polymers formed are low in molecular weight by comparison to other resins. For example, alkyd resins have molecular weights ranging from 1,000 to 7,000 while some vinyl and acrylic resins have average molecular weights in excess of 100,000 and in some cases as high as 500,000.

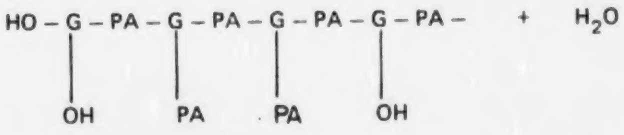
The alkyd polymers also react with oil or fatty acid and are generally classified by the amount of oil or PA used in the formulation, as described below:

	% Oil	% PA
Short Oil	33 to 45	> 35
Medium Oil	46 to 55	30 to 35
Long Oil	56 to 70	20 to 30
Very Long Oil	71 up	< 20

The resulting reactants of the PA, polyol and oil may be represented in part as follows:

PA + $G(OH)_3$ →

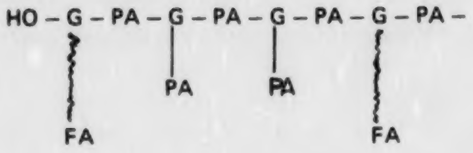
Phthalic Anhydride　Glycerine



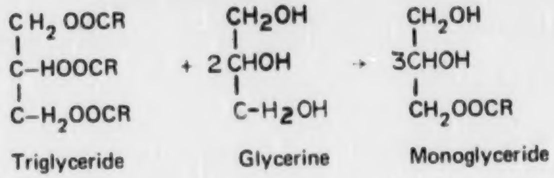
$$\mathrm{HO-\underset{\substack{|\\ OH}}{G}-PA-\underset{\substack{|\\ PA}}{G}-PA-\underset{\substack{|\\ PA}}{G}-PA-\underset{\substack{|\\ OH}}{G}-PA-} \quad + \quad H_2O$$

Glyceryl phthalate　water

This then will react with the long chain oil raw glyceride or fatty acid (~FA) to yield:



Alkyds can be manufactured directly from a fatty acid, polyol, and acid or from the fatty acid oil, polyol, and acid. The second combination (oil, glycerine & PA) produces glyceryl phthalate which is insoluble in the oil and precipitates. This problem can be overcome by first converting the oil to a monoglyceride by heating with a polyol in the presence of a catalyst. This process is called "alcoholysis" of the oil. The basic reaction is shown below:



This is an ester interchange reaction with no loss of water.

When fatty acid rather than oil is used as the starting material, this is called the "one-stage" process. In this process, the fatty acid and glycerine are added to the kettle, the agitator is started and heat is introduced. Sparge gas is turned on to develop an inert atmosphere before the temperature of the batch reaches 300°F where the reaction starts. When the batch reaches 400°F, the PA is slowly added and cooking continued for another 3 to 4 hours until the desired body and acid number are reached.

If the fusion process is being used, a continuous purge of inert gas is maintained to remove the water formed in the reaction. This water may also be removed by what is known as the solvent process. This latter process may also be referred to as the solution process or the azeotropic process. It is similar to the fusion process except that about 10% aromatic solvent (usually xylene) is added at the start. The vaporized solvent is passed into a condenser. The condensate then flows to a decant receiver for separation of reaction water. Recovered solvent is returned to the reactor. Most manufacturers maintain small inert gas flows throughout a solvent cook to prevent air leakage into the reactor system.

A typical manufacturing formula for a 50% oil modified glyceryl phthalate alkyd using the one stage process is given below:[5]

	Actual, lbs	Theoretical, lbs
Phthalic anhydride	39.3	38.7
Glycerol (95% pure)	25.1	21.3
Linseed oil fatty acids	48.5	47.9
Catalyst		
Methyl p-toluene sulfonate	0.2	0.2
	113.2	108.1
Approx. loss	13.2	8.1
Yield	100.0	100.0

The above formulation is based on a 10% excess of glycerol and a manufacturing loss of 5% more than theoretical.

As discussed earlier, when oil is used rather than fatty acid, the alkyds are produced in a two stage process. In the first stage monoglyceride is first produced from the linseed oil and glycerol. Part or all of the polyol is loaded into the reactor. The reactor is purged with inert gas and the agitator and heat turned on. Before the catalyst and oil are added, the reactor is heated to vaporize some polyol so that it can esterify any uncombined PA from the previous batch. If this is not done, the uncombined PA will react with the catalyst and destroy its usefulness. The catalyst and oil are then added and the alcoholysis of the polyol and oil is carried out between 450 and 500°F until the desired end point is reached. This end point is determined by solubility of the batch in methanol. The solubility requirements vary with the type of alkyd being produced. When the alcoholysis is completed, any additional polyol needed is added.

Following this, the required amounts of PA and esterification catalyst are slowly added. If solvent cooling is to be used, the solvent is also added at this time. Cooking then proceeds as before.

A typical manufacturing formula for a 50% oil modified glyceryl phthalate alkyd using the two stage process is given below:[4]

First stage	lb
Linseed oil	51.3
Glycerol (95%)	12.8
Catalyst, $Ca(OH)_2$	0.026

Second stage	
Glycerol (95%)	6.2
Phthalic anhydride	39.7
Catalyst	
Methyl p-toluene sulfonate	0.2
	110.2
Approx. loss	10.2
Solids yield	100.0

Alkyd and other resins are cooked in closed kettles more properly called reactors. They vary in size in commercial production from 500 to 10,000 gallons. A typical reactor system is shown in Figure 3.

They are generally fabricated of Type 304 or 316 stainless steel with well polished surfaces to assure easy cleaning. Design pressure is usually 50 psig. These reactors may be heated electrically, direct fired with gas or oil, or indirectly heated using a heat transfer media such as Dowtherm®. Reactors are equipped with a porthole sightglass, charging and sample line, condenser system, weigh tanks, temperature measuring devices, and agitator. The porthole is used both for charging solid material and for access to the kettle for cleaning and repair.

Good agitation is required for intimate mixing of the reactants and proper heat transfer. A variety of different type blades are used but most are controlled with a variable speed drive. Too rapid an agitation may cause discoloration and too slow an agitation can cause poor heat transfer that will increase heat up time and may cause excessive polymerization due to localized hot spots at the metal-liquid interfaces.

The reactor may be equipped with a variety of different condenser systems. The system shown in Figure 3 includes a packed fractionating column, a reflux condenser and a main condenser. The condensers are water cooled shell and tube type and may be either horizontally or vertically inclined. Vapors are processed and condensed on the tube side and drain to a decant receiver for separation and possible return of solvent to the reactor. A dual function aspirator Venturi scrubber is often added to the system. It is used to ventilate the kettle during addition of solid materials and may also remove entrained unreacted or vaporized solids and liquids from the venting gases.

It is not clear from the literature what kind of production rates, as a function of nominal kettle volume, can be expected from an alkyd reactor. Rather than assume some maximum theoretical production capacity, it was decided to rely on industry experience as determined from some of the

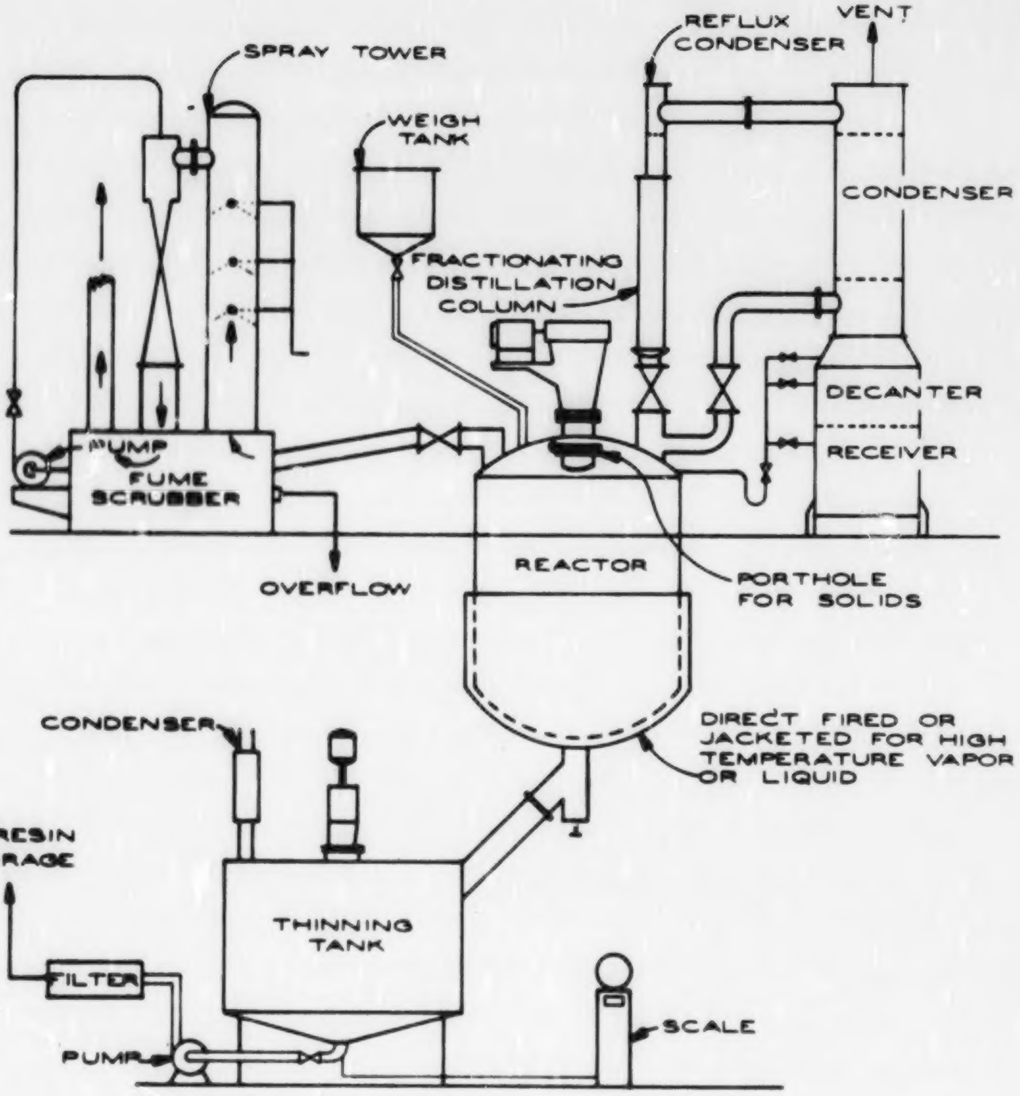


FIGURE 3
MODERN RESIN PRODUCTION SYSTEM
OF
SOLVENT AND FUSION COOKS

questionnaires that were sent out as part of this study.

Questionnaire data from 18 alkyd resin producing plants with 45 alkyd kettles was analyzed in an attempt to determine the effective production capacity of an alkyd resin reactor as a function of kettle volume. Reactor volumes of 400 to 7,800 gallons were reported, with the majority of kettles in the 500 to 2,000 gallon range. Cooking times from 6½ to 29 hours were reported. In the 500 to 2,000 gallon size range, cooking times were well distributed in the 8 to 16 hour range.

In this same size range, production per batch worked out to about 5,000 pounds of alkyd solids per 1,000 gallons of reactor volume. This number possessed a surprising degree of consistency, within reasonable limits, from plant to plant. Assuming a typical density of about 9 pounds per gallon for alkyds, this means that a 1,000 gallon kettle will produce about 550 gallons of alkyd resin in each batch. The larger kettles tended to be filled to a larger fraction of their nominal volume.

Thinning tanks are always included as part of the reactor system. They are normally water cooled and equipped with a condenser and agitator. The partially cooled finished alkyd is transferred from the reactor to the partially filled thinning tank. Since most alkyd resins are thinned to 50% solids, the capacities of these tanks are normally twice the capacity of the reactor. These tanks are also frequently mounted on scales so that thinning solvents may be accurately added.

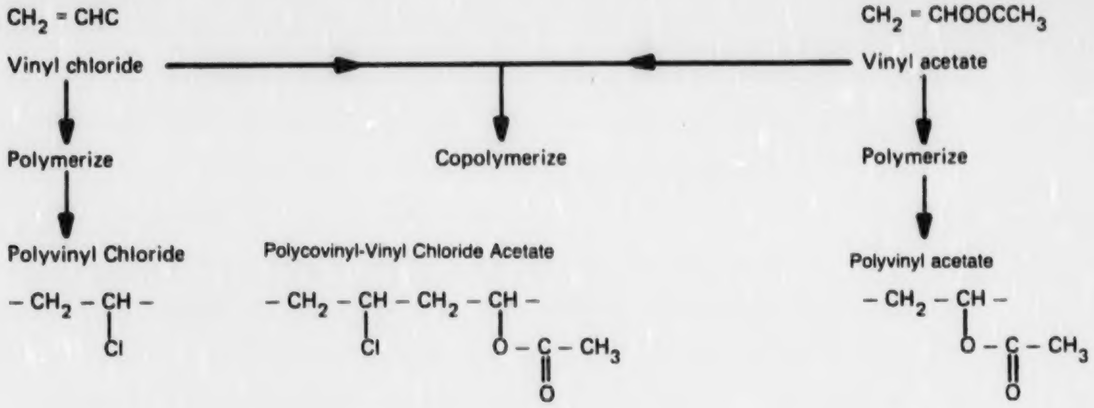
The final step in a reactor system is filtering of the thinned resin prior to final storage. This is normally done while it is still hot. Filter presses are the most commonly used filtering device. Centrifuges are also used. One manufacturer is currently using a continuous "in-line" blending and filtering system for the majority of its resin production. It is not used in all cases, however, due to limitations of the filters.

The manufacturing procedures and equipment used for the production of other resins listed at the beginning of this discussion are quite similar. The major differences are the raw material and process steps utilized. A brief discussion of the other important resin types follows. The technical information contained in these discussions was obtained from Martens' book[4] and the Federation Series on Coating Technology.[2] Economic and production information is from the SRI Chemical Economics Handbook.[3]

Vinyl Resins — Vinyl polymers and copolymers were among the first of the synthetic polymers to gain acceptance as binders for organic coatings. They are available in solution with organic solvents, as high solids dispersions ("organosols" or "plastisols"), as dry powders or as water-borne latexes. Discussion here is restricted to vinyl chloride, vinyl acetate, their related copolymers, and modified types. Following conventional practice other materials like polyethylene, polystyrene etc. are not included although these also contain the basic vinyl building-block group R–CH=CHX.

In 1966 approximately 200 million pounds of vinyl resins were produced for use in surface coatings. Four years later, in 1970 this number had increased by 50% to 300 million pounds. This group of resins is highly versatile and relatively inexpensive. Next to the alkyds it enjoys the largest surface coating use based on volume and sales value. One of the factors responsible for widespread use of these resins is that manufacturers with alkyd kettles were able to adapt these for making vinyl acetate latexes.

Vinyl resins are long molecular chains formed by the addition of vinyl chloride or vinyl acetate monomers. No water or other reaction by-product is formed. The manufacturing chemistry is outlined below.



Monomers comprising the final polymer retain their identity except for the double bonds which largely disappear. The chain length, determined by the number of monomers, is controlled by chain stopping agents or a combination of time, temperature and pressure. The polymerization reaction is highly exothermic and, consequently, heat removal rather than addition is often the problem once the reaction gets started.

There are basically four commercially available manufacturing processes for vinyl resins. Combinations of more than one process, depending upon the end properties desired, is also viable. These are:

1. Bulk polymerization — The monomers are polymerized by themselves (analogous to the fusion process for alkyds). Due to poor heat transfer properties and difficulties in controlling the reaction, this process has lost popularity.
2. Solution polymerization — Vinyl monomers are diluted in solvents containing catalysts. Under controlled conditions this mixture is stirred in an autoclave until the increasing

viscosity (by virtue of molecular size) reaches a predetermined level. When the desired molecular weight range is attained the reaction is stopped. The polymer solution may be used as is, or can be transferred to precipitation tanks where non-solvents precipitate the resin. The several steps involved make this a costly, but nevertheless competitive, method.

3. Suspension polymerization — Small droplets of vinyl monomers containing catalysts are suspended in water and polymerized. Polymerization is initiated within the droplet. This method is used for the manufacture of a greater tonnage of vinyl resin than either of the processes mentioned above. It has largely replaced the first and competes favorably with the second in producing a less costly resin at some expense of quality. The autoclave emulsion product is a suspension of submicron polymer particles and may be marketed in the latex form or the dry resin may be recovered and sold as a powder. The separation of water from submicron particles poses a difficult problem and invariably results in dusting and loss of powder to the atmosphere as fugitive emissions. Resins sold as dry powder are used to prepare organic coating dispersions ("plastisols" and "organosols").

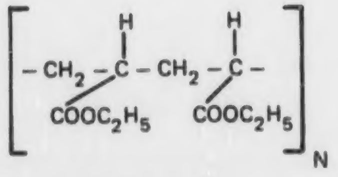
4. Emulsion polymerization — This process differs from the preceding one in that an emulsifier or surfactant is used causing the formation of a very stable fine dispersion of monomer (and consequently of polymer) particles in water. The catalyst is dissolved in the water phase and initiation takes place at the droplet interface. While suspension resins are frequently filtered and dried prior to sale, emulsion polymers are rarely so treated.

Combination methods may employ one of the above processes followed by further chemical treatment to impart additional desirable qualities such as alkyd compatability.

Solvent based vinyl systems require the use of relatively strong, polar solvents. Ketones, nitroparaffins, esters, and some chlorinated solvents can be used. Aromatic hydrocarbons tend to swell the resins but can successfully be used as diluents to reduce costs. Alcohols and aliphatic hydrocarbons are not used.

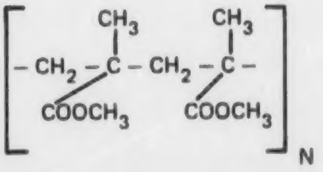
Acrylic resins — Acrylic resins form a group of transparent thermoplastic (or thermosetting if suitably modified) resins formed by polymerizing monomeric esters of acrylic acid or methacrylic acid. Acrylic resins are addition polymers and produce no water or other reaction by-product.

Usage of the term "acrylic resins" is restricted here to resins having the following typical acrylic or methacrylic structures:



(Poly) ethyl acrylate

or



(Poly) methyl methacrylate

Acrylic resins, available in several physical forms, are used in finishes for metal, wood, leather, ceramic and plastic surfaces. Their coatings are characterized by resistance to degradation by UV light, hydrolysis and corrosive chemicals, resistance to mechanical damage and a high quality appearance with aesthetic appeal. Copolymerization with functional monomers is used to control hardness and slip properties, adhesion, solvent resistance and to provide a means for subsequent cross-linking if required. Acrylic polymerization is exothermic and presents a heat removal problem.

The two basic types of acrylic emulsions available are thermoplastic and modified thermosetting. The former is comprised of copolymers of methyl methacrylate with varying amounts of acrylate esters; these are for use in latex paints and in lacquer type finishes. Cross-linking reagents, which react with the functional groups when the film is baked, can be added to produce a thermoset polymer. Films formed in this manner display increased resistance to solvents, chemicals, and greatly improved toughness and hardness at high temperatures.

Manufacturing processes for acrylic resins closely parallel those employed for vinyl resins. These are:

1. Bulk polymerization — Polymerization of undiluted monomer.
2. Solution polymerization — Makes use of a solvent reaction medium in which both monomer and polymer are soluble. This process is used for producing medium-molecular weight resins.
3. Suspension polymerization — The liquid monomer is suspended as droplets in a water medium by vigorous stirring. This technique is restricted almost exclusively to the manufacture of a few powder resins for use in lacquers.
4. Emulsion polymerization — Liquid monomers and surfactant or emulsifying agents are added directly to water. The rate of monomer addition (during the process), the pH and the temperature of the emulsion determine final properties. Water acts as heat transfer medium and a very high molecular weight polymer results. This method is used mostly for water-base acrylic coating resins. In handling by consumers the hazard, odor and

expense of flammable solvents are eliminated.

Monomers used in acrylic resin production include the methyl, ethyl, and n-butyl esters of the acrylates and the methacrylates. These substances are characterized by a low to medium boiling range and by very low odor thresholds. Indeed, odor nuisance is probably the primary air pollution problem associated with acrylic resin production.

Solvent based acrylic systems utilize a variety of solvents. Thermoplastic solution resins are supplied in solvents such as MEK, toluene, or mineral spirits depending on the particular polymer and the intended application. Thermosetting acrylic resins are supplied as solutions in solvents such as xylene, butanol, and ethylene glycol monoethyl ether acetate.

The following items of statistical interest[3] concerning the market for acrylic resins, are offered:

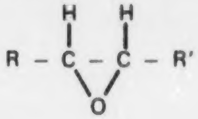
1. In 1970, 220 million lbs of acrylic resins were produced for a value of $85 million.
2. In 1970, these resins accounted for about 13.3% by weight and 16% by value of all synthetic resins, placing them third after alkyds and vinyls.
3. Rohm and Haas Company is the largest producer of acrylics for *latex* paints (65 to 70% of this market in 1971).
4. Of the 14 other producers of acrylics for *latex* paints, only Union Carbide, Celanese Resins, and Thibaut & Walker enjoy any significant sales volume. Most other suppliers in the latex paint industry concentrate their efforts on vinyl resins (polyvinyl chlorides and acetates).
5. Ten paint companies produce acrylic *emulsions* for captive use (including DuPont, Celanese, Glidden, DeSoto, NL Industries, and Sherwin-Williams).
6. In 1971, over 60% of all acrylic *lacquer* was used by General Motors as topcoats for automobiles (other domestic auto makers use thermosetting acrylic enamels).
7. More than 24 companies produce acrylic *enamel* resins (thermosetting solution polymers). The major markets are served by Celanese, Cook Paint & Varnish, DeSoto, DuPont, Ford Motor, Glidden, Inmont, Mobil, PPG, and Sherwin-Williams. These major markets are almost entirely in captive use.

Epoxy resins — Industrial finishes make extensive use of epoxy surface coatings. This popularity is is ascribed to their high resistance to corrosion, strong chemicals, physical abuse, and their adhesion properties.

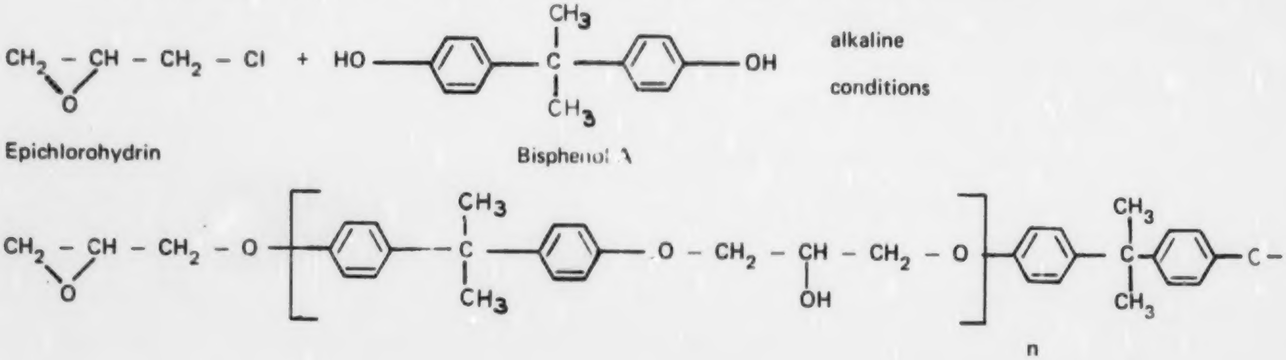
Disadvantages of epoxy coatings, which have curtailed their use in trade sales, are:

1. The need for strong, toxic and/or pungent solvents
2. High cost (although cost per pound, per year of service can be lower than for other resins)
3. Tendency to chalk (loss of gloss) and
4. Appearance

The term "epoxy resin" refers broadly to polymers containing epoxide or oxirane groups:



The most commonly used epoxy resins in surface coatings are the diglycidyl ether type derived from epichlorohydrin and bisphenol A. Manufacturing chemistry is outlined below:



Epichlorohydrin is charged as a liquid to the reactor. The bisphenol A is a dry powder and as such presents a possible dusting problem. The reaction is carried out at moderate temperatures (up to 250°F) and produces HCl as a by-product.

The molecular weight of this entire group of resins is often too low to permit use without a curing process (usually conducted at 140 to 400°F). This results in a two-package, "amine-cured" coating, so named because the curing agents depend on the reaction between the terminal epoxide groups of the epoxy resin and the amine hydrogen atoms of primary or secondary amines.

Among the first curing agents to be used for this application were the aliphatic polyamines DTA (diethylenetriamine) and TETA (triethylenetetramine). These aliphatic amines can lead to dermatitic or respiratory problems where proper precautions and housekeeping practices are not followed during application.

Polyamine adducts provide comparable physical and chemical resistance properties and exhibit lower dermatitic potential and lower vapor pressure than the parent aliphatic polyamine.

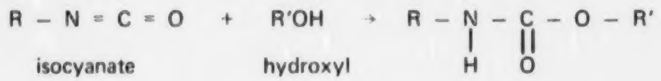
Amine terminated polyamide resins form another major group of curing agents with lower irritation potential. These resins produce a more flexible film with lower chemical resistance than amine-cured films.

Solvents for most unmodified epoxy resins are ketones and esters. Aromatic hydrocarbons are used as diluents. Solvent selection is based on method of application required: brush application requires slow evaporating solvents (e.g. diacetone alcohol, methyl isobutyl ketone) and diluents (e.g. xylene), while spray application calls for faster evaporating solvents (e.g. methyl ethyl ketone) and diluents (e.g. toluene).

In 1970, epoxy coating resin consumption was approximately 80 million pounds; production growth has exceeded a 12% average annual rate compared to a 2 to 3% average for total surface coatings (based on data reported to the U.S. Department of Commerce, Bureau of the Census). Classified as either unmodified or modified (by fatty acids), production can be broken down as:

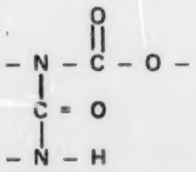
1. Unmodified
    a. Shell — approximately 50%
    b. Dow, Ciba and Celanese, jointly — approximately 40 to 45%
    c. Union Carbide, Reichhold and Resyn — the remainder
2. Modified
    a. For sale only — 21 companies produce modified epoxies for sale, this accounts for 15% of total epoxy resin demand on weight basis.
    b. For captive use — Celanese is the largest producer. Other companies with significant captive consumption include Cook Paint & Varnish, DeSoto, duPont, Inmont Chemical, Mobil, PPG, and Glidden Division of SCM.

Urethane resins — Unlike vinyls and acrylics, urethanes are not polymers made up of monomeric urethane molecules or groups. They are reaction products of isocyanates with hydroxyl-containing materials:

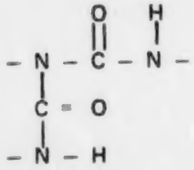


$$\underset{\text{isocyanate}}{R - N = C = O} + \underset{\text{hydroxyl}}{R'OH} \rightarrow R - \underset{\displaystyle H}{\underset{|}{N}} - \underset{\displaystyle O}{\underset{\|}{C}} - O - R'$$

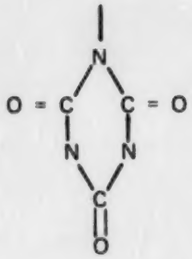
The term "urethane" is used for protective finishes that incorporate a resin containing any of the isocyanate-derived linkages as shown on the following page.



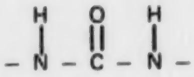
allophanate



biuret

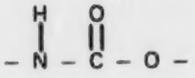


isocyanurate



$-NH-C(=O)-NH-$

urea

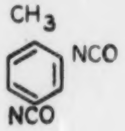


$-NH-C(=O)-O-$

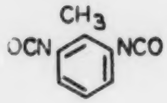
urethane

Polymer formation is accomplished by the use of polyfunctional isocyanates and polyhydroxyl compounds. The primary raw material used for production of urethane coatings are isocyanates, particularly TDI (toluene diisocyanate).

The commercial grade of TDI is usually a 80:20 mixture of the 2, 4 and 2, 6 isomers:



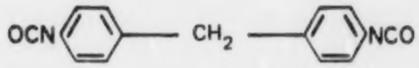
80%



20%

Handling of TDI poses special problems because it has a significant vapor pressure and an irritant effect on the mucous membrane. It has been found[4] that if the unreacted TDI in any prepolymer is kept below 1% of the total product then the amount of TDI vapor released to the air will be at a level considered "safe." Manufacturers are attempting to maintain the free or unreacted isocyanate monomers below this safe level.

Another diisocyanate of commercial importance is 4, 4 — diphenyl-methane-diisocyanate (MDI):



MDI is a solid at ordinary temperatures.

Polyols commonly used included glycerine, glycols, TMP, PE, phenols, and polyethers. Polyesters, alkyds, and castor oil can also be used to supply the hydroxyl groups. A drying oil modified urethane (sometimes called "uralkyds") can be made in a manner similar to alkyds. In this variation the diisocyanate performs the acid function of the phthalic anhydride in linking two monoglycerides. Oil modified urethanes are finding increasing use, especially in trade sales products. These avoid the elaborate curing mechanisms required for the moisture cure, blocked, and two-package formulation types of urethanes.

These materials require strong solvents such as ketones, esters, and aromatics particularly for reactive urethane resins. Adequate ventilation must be provided where these materials are to be handled. Possible alternatives under investigation are coatings without solvents, water emulsion systems and the use of less toxic aliphatic solvents in place of aromatics. This substitution by aliphatics is practical only when total isocyanate content of the resin is below 25%. The oil modified urethanes can utilize mineral spirits and naphtha type solvents.

In comparison to other resins (e.g. alkyds, epoxies, vinyls) urethanes can be formulated to offer a better combination of curing rates, abrasion resistance and water resistance. For an equivalent hardness they are more flexible. Their major drawbacks are cost, yellowing (of urethanes based on aromatic isocyanates), need for strong solvents, and toxicity of some raw materials (as previously discussed).

In the U.S. over 600 companies produce urethane coatings and about 80 companies manufacture urethane resins. Of these, only 22 produce and sell the resins but not the coatings — these account for half of the resin produced. The largest single application for the coatings is in clear wood finishes.

Cellulosic resin — Cellulosic resins are used in the production of about 57% of total lacquers which, by definition, are surface coatings that dry solely by evaporation of an organic solvent (rather than by reaction, such as oxidation or cross-linking, of resin components). Nitrocellulose accounts for 75% of this entire group and is used chiefly as a wood finish. It is easy to apply, low in cost, has excellent intercoat adhesion and solvent release properties. It is also, however, flammable, it yellows and has low chemical resistance.

Cellulosic lacquer resins are manufactured by the esterification of cellulose, a hydrolyl containing compound. For example, nitrocellulose is prepared by nitration of cellulose with nitric acid in the presence of sulfuric acid which removes water formed during the reaction. Manufacturing chemistry is:

$$\text{Cellulose} + HNO_3 + H_2SO_4 \rightarrow \text{Nitrocellulose} + H_2SO_4 + H_2O$$

Cellulose, in the form of cotton linters, is boiled and washed then treated with nitric acid. The reaction product is then treated with ethyl, isopropyl or butyl alcohol (30% alcohol to 70% cellulose), resulting in a highly flammable mixture. Even the recent use of water instead of alcohol as a dampener does not appreciably reduce the hazard potential of handling nitrocellulose. Various safeguards regarding this material are listed in "Handling of Nitrocellulose Manual Sheet N-1" available from the Manufacturers Chemist Association. It may be pointed out that initial interest in nitrocellulose was in the field of explosives.

This group of surface coatings represents a fair vapor emission potential since it is normally used with several volatile materials such as ketones, esters, glycol ethers, alcohols, and other hydrocarbon solvents.

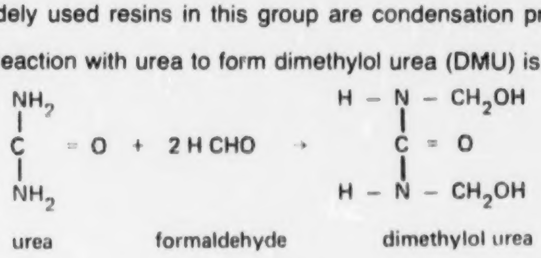
Cellulosic lacquer resins are produced for sale only by Dow Chemical, duPont, Eastman and Hercules. The lacquers themselves call for conventional grinding and mixing operations so most coating producers are capable of manufacturing them.

Cellulosic lacquers can be reformulated with solvent systems considered exempt in many states to accommodate their air pollution laws.

Markets for nitrocellulose lacquers are not expected to show substantial growth due to competition from other coating systems. Cellulose acetate butyrate (CAB) is, however, expected to display moderate growth because of its use in thermosetting acrylic automotive enamels to improve their performance. CAB is produced by reaction of acetic and butyric acids and their anhydrides with cellulose followed by partial hydrolysis.

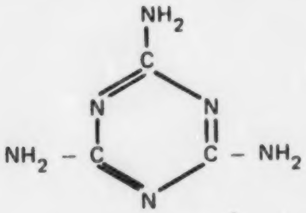
Amino resins — Amino resins are used as a binding or cross-linking agent in the preparation of baking or thermosetting coatings. They can be used in conjunction with alkyds, epoxies, thermosetting acrylics, phenolics and other heat reactive resins. When used in this manner, these resins comprise up to 30% of the total vehicle binding agents. Their use serves to improve baking speed, hardness, solvent and chemical resistance of the film. Reaction occurs primarily with hydroxyl groups present in the polymers to form a cross-linked, thermosetting polymer.

The most widely used resins in this group are condensation products of urea or melamine with formaldehyde. Reaction with urea to form dimethylol urea (DMU) is illustrated:



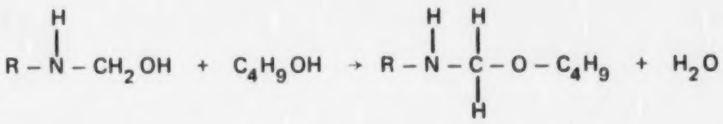
$$\begin{array}{c} NH_2 \\ | \\ C \\ | \\ NH_2 \end{array} = O + 2\,HCHO \rightarrow \begin{array}{c} H - N - CH_2OH \\ | \\ C = O \\ | \\ H - N - CH_2OH \end{array}$$

Reaction of formaldehyde with melamine



proceeds such that the three —NH_2 groups convert to —$N(CH_2OH)_2$ groups to form hexamethylol melamine. Recently methyl ethers of methylol melamine have received much attention with respect to the elimination of organic solvents from baking finishes.

DMU and hexamethylol melamine undergo self-condensation reactions to form polymers with the splitting out of water. The condensation is via methylol groups to yield on ether linkage under alkaline conditions and via interaction between methylol and amide groups to form methylene linkages under acid conditions. For use as coating resins, this self-condensation tendency is blocked by etherification with reactive alcohols such as n-butanol:



$$R-\overset{H}{\overset{|}{N}}-CH_2OH + C_4H_9OH \rightarrow R-\overset{H}{\overset{|}{N}}-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-O-C_4H_9 + H_2O$$

methylol + n-butanol → n-butyl ether + water

Some condensation takes place during etherification. The butylated aminoplast can also undergo further polymerization but only at elevated temperatures. This is the basis for its use in baking systems. The butylated amino resin will also cross-link with hydroxyl containing polymers when acid catalyzed at elevated temperatures. This explains its use as a binding agent in conjunction with other resins in baking finishes. The degree of polymerization allowed during etherification and the amount of combined formaldehyde can be controlled to produce the desired properties.

An example of the preparation of a butylated ether of urea-formaldehyde is outlined by Martens[4] as follows:

"Heat one mole of urea with 2 to 3 moles of slightly alkaline aqueous formalin (pH 8 to 9) to form the methylol derivatives. Add 2 to 3 moles of butanol and adjust with acid to a pH of 3 to 6. Remove the bulk of the water by continuous azeotropic distillation and proceed to an atmospheric distillation for removal of the final traces of water." Amino resins are usually supplied in butanol-xylene solvent systems.

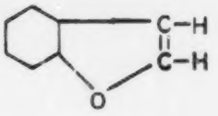
Hydrocarbon resins[5] -- This group is loosely named and includes:

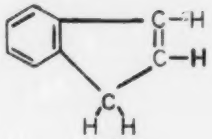
1. Coumarone — Indene Resins
2. Petroleum Resins
3. Styrene — Butadiene Resins
4. Terpene Resins

Together these materials account for a production value roughly equivalent to that of amino resins ($15 million in 1970). Discussion of individual resins is restricted to a brief description.

This group, broadly, covers low molecular weight (under 20,000), thermoplastic resins. Their use is justified by ease of processing, by their neutral hydrocarbon nature, acid-alkali resistance, solubility, and low cost.

1. Coumarone — Indene Resins: these were first produced commercially in the 1920's by polymerization of the fraction of coal tar distillates containing coumarone and indene. Polymerization is conducted in the presence of sulfuric acid (or sometimes aluminum, stannic or antimony chloride) as catalyst. These resins are soluble in aromatic solvents and moderately soluble in petroleum solvents. Structures of coumarone and indene are illustrated:


Coumarone

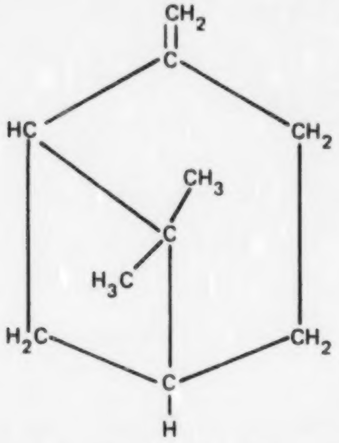

Indene

2. Petroleum resins: are derived from unsaturated hydrocarbons made available from the cracking of petroleum. Because of a strong tendency to form gummy polymers, these resins are undesirable in gasoline and are removed. This ease of polymerization is, however, taken advantage of in the production of resins at low cost. They can be dissolved in solvents and blended with bodied oils for aluminum paints. Monomers for these resins include ethylene, acetylene, butylene, isobutylene, isoprene, and cyclopentadiene.

3. Styrene-butadiene resins: are copolymers containing at least 85% styrene. They are soluble in aromatic hydrocarbons, ketones, and esters. They are not generally compatible with alkyd resins or drying oils; but are compatible with rosin materials and coumarone-indene resins.

4. Terpene resins are produced from compounds derived from the resin of the pine tree.

The most important of these compounds in coating resins is β-pinene:



These resins are soluble in aliphatic hydrocarbons.

All of the monomers used in the various types of hydrocarbon resins are considered photochemically reactive. They contain olefinic and/or cyclo-olefinic types of unsaturation.

Phenolic resins — Among the oldest of synthetic resins, phenolics have been in use since 1910. Although their use in coatings ranks them lower in consumption volume than other groups discussed so far, their total production as a plastic exceeds a billion pounds annually.

Phenolics are condensation polymers obtained by the reaction of a phenol or a substituted phenol with an aldehyde — usually formaldehyde. Depending upon ingredients used, their proportions, catalysts employed, and on reaction conditions, the final form can be a viscous liquid or a brittle solid. Further, these may or may not be heat-reactive.

Phenolics formed in alkaline systems have a high ratio of formaldehyde to phenol ranging from 1.0 to 3.0. In acid systems the ratio lies between 0.7 and 0.9, and the product consists of a thermoplastic or "novalak" (or heat-reactive and non-heat reactive, respectively). A high ratio alkaline catalyst system produces thermosetting resins.

Resins prepared in alkali are of low molecular weight and their coatings on metal tend to eyehole and crawl; phenolics formed in acid medium require the addition of curing agents which limit their shelf life. Ammonia or amine catalyzed phenolics become the normal choice. These, when cured, have an attractive gold color found in can linings. Most phenolic resin coatings comply with Food and Drug Administration regulations concerning safe linings of food containers.

Manufacture of phenolics calls for ordinary stainless steel kettles designed to withstand

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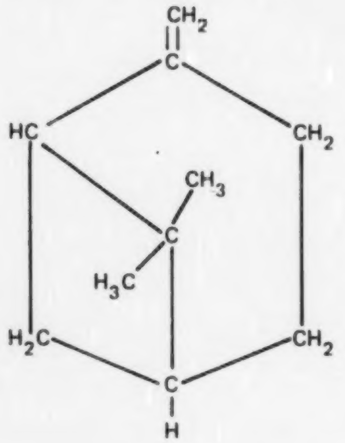

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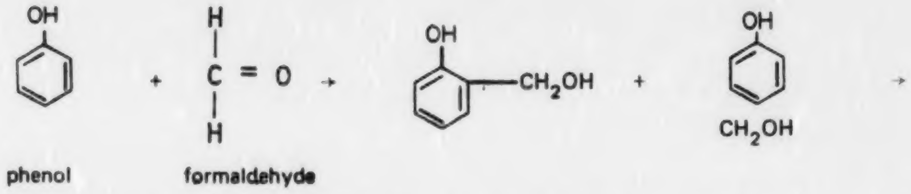
Manufacture of phenolics calls for ordinary stainless steel kettles designed to withstand both vacuum and moderate pressure and equipped with reflux condenser and dumping hatch.

The chemistry of phenolic resin production is illustrated below:



The $-CH_2OH$ groups can react with available ortho or para hydrogens on phenolic rings or with other $-CH_2OH$ groups. Either way, a molecule of water is formed.

Most of the commercial phenolics use formaldehyde as the source of the aldehyde groups even though, in theory, many aldehydes are suitable. Formaldehyde is a gas at ordinary temperatures but is usually supplied commercially in 37 to 50% aqueous solutions.

Besides phenol, a few substituted phenols are used. These include p-cresol, p-phenylphenol, p-tert-butylphenol, and bisphenol A. Only the *para* forms of the above compounds are used since the *ortho* and *meta* forms produce polymers of poorer quality.

Solvents used for phenolics include alcohols, ketones, esters, and glycol ethers.

Silicone resins — Silicone resins are generally supplied as solutions in aromatic hydrocarbon solvents which are included in manufacture to improve control of hydrolysis and prevent gelation. Aliphatic hydrocarbons and alcohols may also be used; ketones and esters are seldom required.

Silicone resins exhibit excellent color and gloss retention even at 500°F. They can be copolymerized to improve properties of other resins at elevated temperatures. They also exhibit excellent external durability. These two properties are responsible for their position in the coatings industry.

The manufacture of silicone resins begins with the production of chloro-substituted silanes. Several methods are available, all of which produce mixtures of various alkyl-chloro substituted products (such as $(CH_3)_4Si$, $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_4). These are separated by fractional distillation.

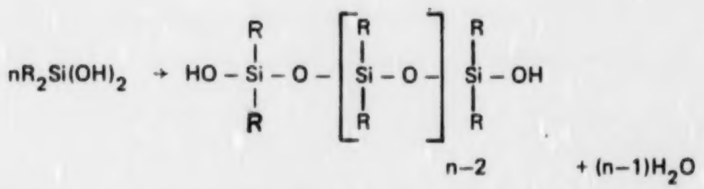
The next step is the preparation of silanols as, for example,

$R_3SiCl + H_2O \rightarrow R_3SiOH + HCl$

$R_2SiCl_2 + 2H_2O \rightarrow R_2Si(OH)_2 + 2HCl$

$RSiCl_3 + 3H_2O \rightarrow RSi(OH)_3 + 3HCl$

This is followed by the polymerization of the polyfunctional silanols:



$$nR_2Si(OH)_2 \rightarrow HO-\overset{R}{\underset{R}{Si}}-O-\left[\overset{R}{\underset{R}{Si}}-O-\right]_{n-2}\overset{R}{\underset{R}{Si}}-OH + (n-1)H_2O$$

Monofunctional silanols are used to terminate the chain while trifunctional silanols can be used as cross linking agents.

Silicone resins can be used as such but are often combined with other vehicles either as a blend, or, better, as a copolymer. A commonly used copolymer is that made with alkyds. The alkyd can either be cooked separately and then copolymerized with a methoxy or hydroxy functional silicone intermediate; or the alkyd raw materials and the silicone intermediate can be charged together and cooked in a single step.

Another important copolymer group is the silicone-acrylic copolymer emulsions. These are used mainly for exterior house paint and maintenance coatings. This concludes the discussion of the resin types.

As may be surmised from the preceding discussions, paint manufacturing can be summarized as a raw material and finished products handling problem with a variety of intermediate batch operations. The inter-relationship of all these operations is schematically illustrated in Figure 4. As paint manufacturing has developed into a specialized branch of the chemical process industry, the quantity and number of raw materials and finished products have increased significantly. The industry, however, has been able to maintain the price of finished product by increased batch size, by more efficient use of labor, and, most importantly, through improved material and product handling.

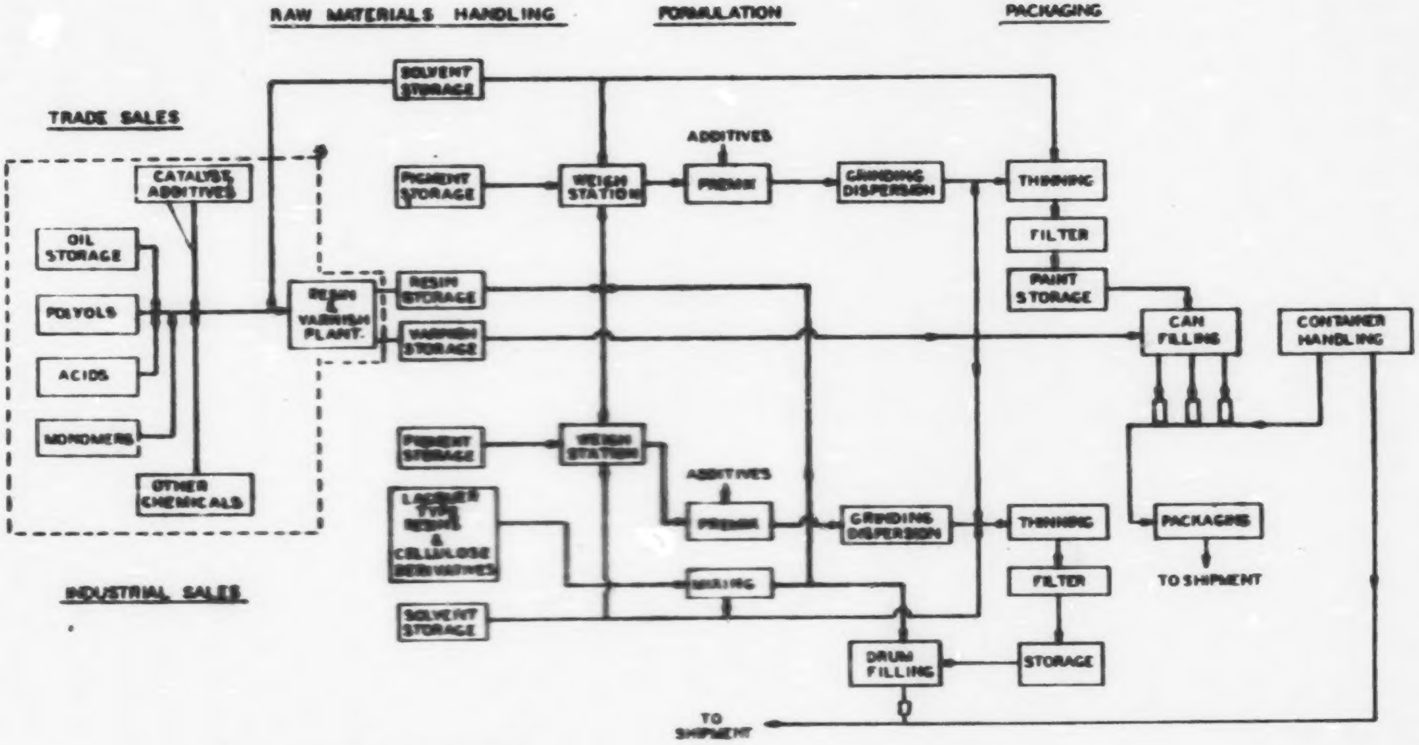
Usually, plants that produce many of their own resins and manufacture a variety of trade and industrial products are divided into the general areas indicated on Figure 4. This simplifies handling of solid materials and solvents which vary for each type of operation. This is also true for packaging of the finished products.

The early paint plants were normally built in four story buildings to allow for gravity process flow. Vehicles and solid were stored on the top floor in tanks and bags. Mixing of pigments and vehicles took place on the third floor; the grinding or dispersion occurred on the second floor; and the filling packaging, warehousing, and shipping took place on the first floor.

New paint plants are now designed differently from earlier facilities. They can be a single story open building with or without a mezzanine or a three story plant laid out on a hillside. The

FIGURE 4

MATERIALS FLOW SHEET FOR PAINT MANUFACTURING



*. MANY PLANTS PURCHASE
RATHER THAN MANUFACTURE
THEIR RESINS AND VARNISHES

major impetus for this change was handling and warehousing of raw material as well as finished stock. This is done entirely on the ground floor using fork trucks, conveyors and storage racks. The hillside three story building meets these requirements, since the top story is also a ground floor. Processing is then done on the second floor and filling and warehousing on the lower level. Material flow is also conducted by gravity and this arrangement is probably the best.

B. Process Data From Questionnaires

A primary source of information for this study will be the Paint and Varnish Industry Questionnaire which has been distributed to a sampling of the industry. The questionnaires were distributed under authority granted the U.S. Environmental Protection Agency by Section 114 (a) of the Clean Air Act.

Several criteria were considered in selecting those plants which would receive a questionnaire. These included:

1. Geographical location
2. Type of products
3. Plant size
4. Presence of air pollution control equipment
5. Total output
6. Number of plants

The list of plants which were chosen represents a compromise with respect to the above-mentioned criteria. The nature of the coatings industry is such that it is difficult, if not impossible, to obtain a sample population which is representative of the industry according to all of these criteria. If, for instance, one were to obtain a representative sample according to plant size, the result would be a very poor sample with respect to production volume. The aim, then, was to obtain a list of plants which would provide the desired information and yet provide at least "adequate" representation with respect to the guidelines set forth above.

Table 2 contains a breakdown of the way the questionnaires were distributed. This table reflects the groups as they were sent out.

The "Resin List" was taken from the NPCA *Raw Materials Index – Resin Section*.[6] The *Index* listed 59 companies which produced paint resins for sale. It includes some companies which produce finished coatings as well as resins but does not include companies which produce resins for internal use only. Of the 59 companies, 32 were chosen on the basis of diversity of product and amount of output. Plant locations were obtained from the companies themselves or, for those companies which would not release that information, from the *Chemical Economics Handbook* of the Stanford Research Institute[3] or the *Paint Red Book*.[7] A total of 55 plants were selected. Where a company had more than a single plant, about half its plants were chosen.

A list and description of the 200 largest paint companies is contained in *Kline's Marketing Guide to the Paint Industry*.[1] These 200 companies account for about 88% of the industry output. From this list 139 large companies were selected. These were further subdivided into single plant companies and 31 multi-plant companies. As before, each of the 31 companies that had more than one plant had questionnaires sent to about one half of its plants resulting in a total of 75 questionnaires. Many of the plants in this group produce resin as well as paint.

The "small" plant list was obtained from a list of its "A" members supplied by the National Paint and Coating Association. The companies were classified by the NPCA into very general categories according to size, percent trade or industrial, and product type. This list was used to obtain a sample of small producers. In the NPCA classification accompanying the membership list, "small" was defined as having sales of less than 5 million dollars. A sample of 198 companies classified as small was selected. Only two of these companies were included in the 200 largest companies described in *Kline's*. The smallest of these two had sales of 1 to 2 million dollars. Because of the nature of the paint industry, it is likely that these 198 companies average considerably less than one million dollars in sales. As far as could be determined at the time, none of these plants produced resins. This has been substantiated by the questionnaires received.

Finally, another 16 plants from 13 companies were selected. They were included on the basis of reports that they contained air pollution control devices. Since one of the purposes of the questionnaires was to obtain cost effectiveness information on such devices, effort was made throughout to locate plants with control equipment. For this reason, a somewhat disproportionate share of those plants in geographical areas known to have a history of vigorous pollution control legislation received questionnaires.

Table 3 contains a geographical breakdown of the categories as listed in Table 2. Table 4 presents a percentage distribution by geographical regions for the entire questionnaire sample compared to the distribution of all plants and of value of shipments for the entire industry.

Examination of Table 4 indicates that the mid-Atlantic region is somewhat under-represented. A large part of this under-representation can be traced to the "small" plant list. It is felt that this will not materially affect any conclusions which might be drawn from the questionnaires as a group.

TABLE 2

QUESTIONNAIRE DISTRIBUTION

Type	Companies	Plants
Resin	32	55*
Marketing Guide		
(a) Multi-plant	31	75
(b) Single plant	108	108
Small	198	198
Other	13	16
Total	382	452

*Ten of these plants also manufacture coatings.

Questionnaire Returns

A total of 338 questionnaires have been returned in time to be used in this study. As each one was received, it was placed into one of the three categories outlined below.

Plant Type	Production	Questionnaire Received
1	Coating and Resin	76
2	Coatings only	223
3	Resins only	39

In addition 22 questionnaires have been withheld by the Environmental Protection Agency due to requests for confidentiality and are not included in the above. Another 13 plants, by mutual agreement, were not required to return the questionnaire since it did not properly apply to their situations. The 338 returns used amount to 75% of the total mailed.

1. Raw Materials

Table 6 lists raw materials used by the respondent plants. All quantities are in million pounds per year. Broad categories covered are oils, polyols, acids, monomers, purchased resins, pigments and extenders. Solvents, due to their importance in air pollution, are covered in a separate table.

Among the oils, usage of linseed exceeded that of soybean oil, for responding plants, by a much smaller margin than in industry-wide figures. Linseed is a drying oil but it yellows whereas soybean oil is semi-drying and resists yellowing. Usage of these two oils, for the 338 plants was about 95 million pounds and 82 million pounds respectively. Approximately one-fourth of the total oil was used in production of resins by type 3 plants. Sixteen percent is used by type 2 plants for production of coatings. The remaining 56% is used by type 1 plants for both resin production and coating production.

The primary usage of polyhydric alcohols, or polyols, is in the production of resins by the esterification reaction with an acid. Glycerol or glycerine, first obtained as a by-product of soap manufacture, is used in short and medium oil alkyds. Pentaerythritol, with four hydroxyl groups, is used primarily in long oil alkyds. These two polyols are used in quantities of 22.7 and 36.1 million pounds, respectively. Ethylene and propylene glycols are the lowest cost polyols available and their use in type 2 plants (which do not produce resins) is largely as an "anti-freeze" agent. "Other" polyols listed include trimethylolethane and sorbitol.

TABLE 3

GEOGRAPHICAL DISTRIBUTION OF QUESTIONNAIRES

Location	Resin	Multi-Plant	Single Plant	Small	Other	Total
New England Me., Vt., N.H., Mass., R.I., Conn.	3	2	3	15	2	25
Mid Atlantic N.Y., Pa., N.J.	11	13	24	23	5	76
East No. Central Wis., Mich., Ill., Ind., Ohio	14	20	33	54	4	125
West No. Central N.D., S.D., Neb., Kan., Minn., Ia., Mo.	1	3	13	13	0	30
South Atlantic Md., Del., W.Va., Va., N.C., S.C., Ga.	3	8	12	22	0	45
East So. Central Ky., Tenn., Miss., Ala.	8	4	6	12	0	30
West So. Central Tex., Okla., Ark., La.	4	6	5	15	1	31
Mountain Mont., Id., Wyo., Nev., Utah, Colo., Ariz., N. Mex.	0	1	2	7	1	11
Pacific Wash., Ore., Cal.	11	18	10	37	3	79
	55	75	108	198	16	452

TABLE 4

PERCENTAGE DISTRIBUTION OF QUESTIONNAIRES, PAINT PLANTS, AND VALUE OF SHIPMENTS

Region	Questionnaires %	Number of Plants* %	Value of Shipments* %
New England	5.5	5.8	2.8
Mid Atlantic	16.8	26.1	23.4
East No. Central	27.7	23.6	35.0
West No. Central	6.6	6.3	6.5
So. Atlantic	10.0	10.3	7.5
East So. Central	6.6	3.2	4.6
West So. Central	6.9	6.6	6.2
Mountain	2.4	1.5	0.6
Pacific	17.5	16.6	13.4
	100.0	100.0	100.0

*Source: 1967 Census of Manufacturers

TABLE 5

INDUSTRY QUESTIONNAIRE — TABULATION SUMMARY

	Type 1	Type 2	Type 3	All Types	1970 Industry Total[3]
Number of Plants in Sample	76	223	39	338	
Products & Production					
Major Products (MM gal)					
Paints — oil/solvent base	98.32	77.01		175.33	
Paints water base	49.28	43.86		93.14	
Varnishes	21.43	1.10		22.53	
Lacquers	12.07	23.16		35.23	
Total	181.10	145.13	—	326.23	830
Trade sales	108.66	77.45		186.11	430
% of total sales	60	53		57	52
Major Resins and Varnishes Produced (MM lb)					
Alkyd	299.15		191.32	490.47	
Acrylic	51.07		114.03	165.10	
Polyester	28.76		67.50	96.26	
PVA	48.72		27.93	76.65	
PVC	0.03		63.50	63.53	
Epoxy	49.88		12.84	62.72	
Urethane	4.21		1.79	6.00	
Cellulosic	2.18		14.76	16.94	
Amino	19.42		24.03	43.45	
Rosin	0.65		24.68	25.33	
Styrene	15.79		0.60	16.39	
Phenolic	3.16		—	3.16	
HC	0.08		38.00	38.08	
Other	29.67		40.89	70.56	
Total	552.77		621.87	1,174.64	1660
Varnish Total	18.68		37.74	56.42	
Separately packaged solvents	17.07	8.41	—	25.48	

TABLE 6

INDUSTRY QUESTIONNAIRE — TABULATION SUMMARY

Raw Materials Used (MM lb)

Oils	Type 1	Type 2	Type 3	All Types
Castor	5.71	2.15	0.85	8.71
Cotton Seed	0.02	0+	0+	0.02
Linseed	47.37	29.43	18.12	94.92
Safflower	6.01	1.44	5.02	12.47
Soya	56.05	1.99	23.55	81.59
Tung	5.51	0.93	1.37	7.81
Tall	27.72	0.02	18.68	46.42
Fish	0.81	1.73	0.56	3.10
Coconut	0.60	—	0.83	1.43
Other	8.87	7.54	8.41	24.82
Total	158.67	45.23	77.39	281.29
Polyols				
Glycerol	16.07	0.02	6.64	22.73
Ethylene glycol	12.53	7.95	4.54	25.02
PE	21.80	0.04	14.22	36.06
TMP	2.20	—	0.57	2.77
PG	9.38	2.52	12.87	24.77
Other	14.84	1.35	4.16	20.35
Total	76.82	11.88	43.00	131.70
Acids				
PA	61.69		42.86	104.55
IPA	7.38		4.82	12.20
MA	4.47		6.25	10.72
Benzoic	2.37		0.11	2.48
Adipic	0.77		0.49	1.26
Other	7.02		10.56	17.58
Total	83.70	—	65.09	148.79

TABLE 6 (continued)

Monomers	Type 1	Type 2	Type 3	All Types
Styrene	24.85		43.68	68.53
Vinyl Toluene	2.89		10.66	13.55
Acrylic Esters	51.96		21.63	73.59
Vinyl Acetate	13.42		16.23	29.65
Vinyl Chloride	—		60.39	60.39
Other	13.91		95.21	109.12
Total	107.03	—	247.80	354.83
Resins Purchased				
Alkyd	46.25	163.93	3.46	213.64
Acrylic	46.00	44.67	—	90.67
Polyester	5.20	10.30	0.06	15.56
PVA	27.15	54.06	0.02	81.23
PVC	11.34	12.25	11.25	34.84
Epoxy	27.66	12.74	1.54	41.94
Epoxy	27.66	12.74	1.54	41.94
Urethane	0.89	0.83	—	1.72
Cellulosic	6.43	15.36	—	21.79
Amino	13.15	10.19	1.00	24.34
Rosin	1.70	1.05	1.59	4.34
Styrene	10.01	0.92	0.04	10.97
Phenolic	2.25	0.88	2.95	6.08
HC	1.72	1.49	1.51	4.72
Other	36.01	31.85	1.44	69.30
Total	235.76	360.52	24.86	621.14
Pigments				
TiO_2	168.77	137.24		306.01
Iron Oxide	16.18	14.34		30.52
Zinc Oxide	17.06	10.13		27.19
Zinc Chromate	2.54	3.19		5.73
Chromium	1.64	1.55		3.19
Metallic	5.11	19.56		24.67
Lead Chromate	10.60	8.37		18.97
Other Lead	6.93	7.75		14.68
Cadmium	0.07	0.12		0.19
Iron Blue	0.06	0.08		0.14
Other Inorganic	6.30	5.56		11.86
Total Inorganic	235.26	207.89	—	443.15

TABLE 6 (continued)

	Type 1	Type 2	Type 3	All Types
Carbon blacks total	1.08	1.02	—	2.10
Organic total	7.42	2.58	—	10.00
Extenders total	247.36	245.88	—	493.24

Acids are used in conjunction with polyols for resin production and are, therefore, not purchased by type 2 plants. Phthalic anhydride is used in alkyd production, because being an acid anhydride it has a fast reaction rate and produces minimum water. It accounts for 70% of the usage or 104.5 million pounds. Isophthalic acid and maleic anhydride add another 10 to 12 million pounds each. "Other" acids include fumaric and succinic acids.

Monomers provide individual molecules, acting as basic "building blocks", for polymers which form unmodified resins. Significant quantities of monomers, other than those listed in the questionnaire, were tabulated — the list has been expanded to include vinyl acetate and vinyl chloride. In addition, "other" monomers are comprised mainly of the group indene, cyclopentadiene and methyl cyclopentadiene. Usage of all monomers by type 3 plants is substantially higher than for type 1 plants. This relationship is also reflected in the production of vinyl and acrylic resins, in Table 5.

Approximately 34% of all purchased resin quantities are alkyds. This quantity obviously does not represent the total consumption of alkyds by these plants. Since type 1 plants satisfy some of their own needs for resins, while marketing other quantities and purchasing still others, it is impossible to correlate production and consumption by resin types between Tables 5 and 6. Quantities purchased by type 3 plants are intended for reformulation or merely to complete a product line in resale. These purchases are small, with the exception of polyvinyl chloride which accounts for better than half of their purchases.

Of the 31.8 million pounds "other" resins purchased by type 2 plants, almost 3 million pounds were reported as asphalt, another 1.3 million pounds as chlorinated rubber and paraffin and about 1 million pounds of vinyl acrylic. Similarly, 4 million pounds of vinyl acrylic contribute to the 36.0 million pounds "other" resins purchased by type 1 plants.

The purposes of hiding, protection, and decorating a surface is served by pigments. Hiding can be accomplished by white, opaque, pigments which reflect all wavelengths of incident light and decorating by non-hiding pigments which impart a color to the coating by reflecting only a select portion of the spectrum. In other cases, the color pigment has sufficient hiding power alone. It can be seen from Table 6 that almost 71% of the inorganic pigments are titanium dioxide which has an extremely high refractive index. Despite its higher cost per pound it is more economical per unit hiding power.

Use of lead pigments, which at one time enjoyed great popularity, has been declining substantially due to the availability of higher hiding pigments such as TiO_2. Recent legislation has also affected usage in trade sale finishes. A fair number of responding plants commented pertaining to their use of these pigments. These comments included ". . . discontinued use. . .", "Other lead . . . to be discontinued . . .", ". . . in traffic paint only.", and ". . . have phased out . . .". In all, planned and implemented discontinuations in use of lead pigments accounted for 3% of this group; current usage in traffic paints for 7.7%.

Raw materials listed under "extenders" include such items as talc, ground calcium carbonate, silica, kaolin, barytes and mica. These materials, generally, have low refractive indices and little hiding power by themselves but used in combination they provide important properties at low cost. Extenders also permit the use of smaller quantities of higher cost pigments. Table 6 indicates that usage of extenders actually exceeds that of pigments, by a small margin.

Table 7 presents a summary of solvent consumption by plant type as determined from the questionnaire responses. Respondents were asked to report their solvents by group as follows:

1) Ethers
2) Olefinic ethers
3) Esters
4) Olefinic esters
5) Alcohol
6) Olefinic alcohol
7) Aromatic (Toluene & Xylene)
8) Branch chain ketone
9) Straight chain ketone
10) Olefinic ketone
11) Solvents containing a combination of hydrocarbons, alcohol, esters, ethers, or ketones having an olefinic or cyclo-olefinic type of unsaturation of 5% or more.
12) Solvent containing a combination of aromatic compounds with 8 or more carbon atoms to the molecule, except ethylbenzene, of 8% or more.
13) Solvent containing a combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene, or toluene of 20% or more.

Grouped solvents which make up less than 5% of the total solvents could be lumped together under "Other Solvents".

These classifications were based on the Los Angeles County Rule 66 type definition of photochemically reactive solvents. Under this definition groups 2, 4, 6 to 8, and 10 to 13 are considered photochemically reactive. This classification is used in a modified form in Table 7. Groups 2, 4, 6, and 10 were reported in such minimal quantities that they have been simply included in a separate category "Other Photochemical". Difference between "Rule 66" and the classification system used here are found in categories 11, 12, and 13. Rule 66 considers solvents to be reactive if they contain *more than* 5%, 8%, or 20%, respectively, of the objectionable substances.

TABLE 7

SOLVENT USAGE, (MM lb/yr)
(Questionnaire Data)

	Type 1	Type 2	Type 3	Industry Total[3]
Ether	4.28	4.59	1.11	
Ester	25.60	23.29	8.63	350
Alcohol	35.32	25.59	51.10	550
Aromatic	221.99	105.72	63.05	800
Ketone (Branch Chain)	15.27	9.53	3.10	800
Ketone (St. Chain)	50.04	28.38	7.83	
Group 11	0.94	11.36	7.50	
Group 12	89.94	27.60	5.68	
Group 13	2.66	6.23	0.75	
Mineral Spirits — Naphtha	70.11	49.25	17.04	
Other Non-photochemical	72.83	39.73	22.51	
Other Photochemical	4.28	0.95	6.56	
Other	117.83	19.38	10.76	
Photochemical	335.08	161.39	86.64	
Non-photochemical	188.07	121.58	91.18	
Unknown	187.94	68.63	27.80	
Total	711.09	351.60	205.62	3390

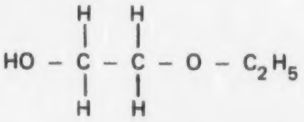
	MM lb	%
Summary:		
Photochemical	583.11	46.0
Non-photochemical	400.83	31.6
Unknown	284.37	22.4
Total	1,268.31	100.0

The present system includes the 5%, 8%, and 20% levels, respectively, in the reactive category.

The mineral spirits — naphtha group was added to accommodate the large quantities of solvents reported as such. A qualification applies, however. If a solvent was reported as simply mineral spirits it is included in this group. However, if a solvent is defined as "exempt" mineral spirits (or naphtha, VMP, etc.) it is included in the category "Other Non-photochemical". The category "Mineral Spirits — Naphtha" no doubt contains material which could be classified photochemical according to the above definition as well as material which is non-photochemical.

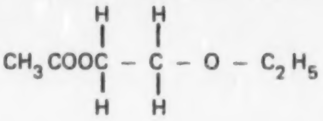
Some companies reported solvents as simply "aliphatic". These were also included in the group "Other Non-photochemical".

The "Cellosolve®" type solvents present some difficulty in classification. A series of glycol ethers and esters of glycol ethers find extensive use as solvents. These are commonly known as "Cellosolves®" due to their use as solvents for Cellulose® derivatives. One such compound, ethylene glycol monoethylether has the following structure:



$$\mathrm{HO}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{O}-\mathrm{C_2H_5}$$

An ester derivative of this, ethylene glycol monoethylether acetate has the structure:



$$\mathrm{CH_3COO}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{O}-\mathrm{C_2H_5}$$

The first of these compounds, Cellosolve®, could be classified as either an alcohol or as an ether. For the purpose of this study Cellosolve® and its related compounds (e.g. methyl Cellosolve®, butyl Cellosolve®, etc.) are classed as ethers.

The second of the above structure, Cellosolve® acetate, could be classed as an ether or as an ester. For this study, Cellosolve® acetate and related compounds (e.g. butyl Cellosolve® acetate, etc.) are considered esters.

Table 7 also contains totals with respect to photochemical properties. The "unknown" group includes the "other" category as well as the mineral spirits — naphtha. Solvents that can definitely be classed in photochemical groups make up 46% of the total. The largest single group of solvents is the aromatics (toluene and xylene) which make up 31% of all solvents used.

It was often necessary to convert from data reported in gallons to a weight basis. Where a specific compound was reported it was possible to use an actual density from the literature. Where mixtures or general classes were listed, an average value for solvents of the particular type was used. Some representative conversion factors for mixtures and general classes are listed as follows:

Solvent	Pounds/Gallon
Alcohols	6.7
Ketones	6.7
Esters	7.3
Aromatic	7.24
VMP Naphtha	6.3
Mineral Spirits	6.5

For solvents listed under "other" a value of 7.0 pounds/gallon was used.

Two other categories of material that have been listed in the questionnaire are drying agents and mercury compounds. These are used in relatively small quantities, but may be important from an environmental standpoint.

Drying agents are usually organic acid salts of lead, cobalt, zirconium, manganese, or calcium. Lead based driers have historically been the most common. However, this is in the process of changing due to increasingly stringent regulations on lead content. The questionnaire responses, unfortunately do not list separate drier categories.

Mercury compounds, usually phenyl mercury based, are used as preservatives and fungicide. Limitations on mercury content in paint are presently under consideration by various groups. Usage of mercury compounds and drying agents as reported in the questionnaire is summarized in Table 8.

2. Products and Production

In the Industry Questionnaire, production of coatings was broken down by oil/solvent base paints, water base paints, varnishes and lacquers. Similarly resin production was reported by fourteen major types. Production of coatings is in million gallons and that of resins in million pounds. A summary of the production data tabulated is presented in Table 5. As described earlier, type 1 plants produce both coatings and resin, type 2 plants produce coatings only, and type 3 plants produce resins only.

Total coatings production for the plants included in the table amounts to somewhat over 30% of the industry's 1972 production — total production estimated to be 930 million gallons based on *Current Industrial Reports* (and estimates for December 1972). This 30+% of the total represents a broad sample of plants since the emphasis in selecting was on diversity of plant type and size.

TABLE 8

DRYING AGENTS AND MERCURY COMPOUNDS
(Questionnaire Data)

Type of Plant	Drying Agents (lb/yr)	Hg Compounds (lb/yr)
1	6,427,484	695,977
2	4,399,769	637,878
3	46,892	1,898
Total	10,874,145	1,335,853

Emphasis, in this sample, on plants with emission control devices skewed the distribution towards larger plants which resulted in a sample consisting of 18% of all plants but 30% of all coatings production. More than half of the coatings for type 1 and type 2 plants are oil/solvent base which is fairly typical of the industry.

While trade sale finishes accounted for 49% of U.S. production in 1972, plants in Table 6 indicate that 57% of their products fall into this category. This results from including in the sample a few very large type 1 plants specializing in sales to the consumer rather than to industry.

Table 5 also shows products and production under the category of resins and varnishes. Although alkyd resins are facing increasing competition from acrylics, epoxies, polyvinyl acetate and polyurethanes they still account for about 50% of all resins produced and consumed. Less than 10% of the alkyds produced find uses in areas other than coatings. Production of alkyd resins is distributed about equally in the industry between plants making resins only and those that produce both resins and coatings. In our sample, however, distribution of alkyd production is weighted towards those making both. Type 3 plants, on the other hand, produce substantially larger quantities of acrylic, polyester, polyvinyl chloride, amino and hydrocarbon resins than do type 1 plants.

The largest single component in the "Other" resins category is vinyl acrylic amounting to 20 million pounds or almost one-third of the production listed under this subtitle. The remainder is comprised of small volume resins such as chlorinated rubber, asphalt, silicones, and natural resins.

3. Process Equipment

a. Dispersion and Grinding Equipment — The principle manufacturing steps involved in producing a finished coating from raw materials consist of various types of milling and dispersion steps. Milling consists of a reduction in the size of the primary pigment particle. Dispersion consists of a deagglomeration or separation of aggregates of individual particles, wetting of particles and agglomerates, and a uniform distributing of particles throughout the liquid phase. Pebble and ball mills accomplish size reduction as well as dispersion. Roll and sand mills are primarily used for dispersion. Various types of high speed dispersers, disc impellers, etc. are used for dispersing easily dispersed pigments. A final category of simple mixers or blenders is employed for such purposes as thinning, shading, and other finishing operations.

A portion of the questionnaire was devoted to a listing of such devices. A summary of this information is presented in Table 9. A problem exists here of terminology. The terms "mills", "mixers", "dispersers", etc. often have imprecise meanings as far as every day usage in the paint

TABLE 9

MILLS, MIXERS, ETC.
(Questionnaire Data)

	Number		
	Type 1	Type 2	Type 3
Roll	126	152	5
Pebble	336	506	0
Sand	299	289	5
Ball	382	282	1
Other	2741	2043	128

industry is concerned. The roll, pebble, sand and ball mills have a definite meaning to most people and it is felt that these have been reported in an unambiguous manner. The "other" category apparently includes an undetermined, but perhaps large, degree of duplication. In many cases, the same unit is apparently listed as, for instance, a "mixer" in one part of the questionnaire and as some other type of device in another part. The numbers reported in the "other" category are probably too high for reasons outlined above.

b. Solvent Storage Tanks — The questionnaires requested data on all solvent tanks over 5,000 gallons covering size, turnover, type of solvent, vapor pressure, and type of control if any. A summary of total number of tanks, number of uncontrolled tanks, and turnover is given in Table 10. Uncontrolled tanks comprise 41% of the total. Total quantity of solvent handled in 5,000 gallon or larger tank can be calculated to equal 1,130 million pounds a year using a density of 7 pounds/gallon. This represents 89% of the total consumption of 1,268 million pounds reported earlier in Section 1.

Controlled vents, as reported in the questionnaires, consisted almost entirely of conservation vents. In general, tanks containing high vapor pressure solvents were more likely to have conservation vents though this was by no means universally observed. Filling losses are relatively unaffected by use of conservation vents. Vapor losses during filling operations are proportional, on a weight basis, to the product of vapor pressure and molecular weight. Some theoretical filling losses have been calculated for some selected solvents and are given in Table 11. The calculation assumes that the gas displaced from the tank being filled is saturated with the solvent in question at a temperature of 20°C. A pumping rate in excess of 144 gal/min for toluene will give an instantaneous emission rate in excess of the 8 lb/hr limit often invoked for photochemically reactive solvents. Whether this is in violation depends on local interpretation of local regulations and is beyond the scope of this section. It can be pointed out that these losses represent a very small percentage of the solvent being handled. On the other hand, a given quantity of solvent undergoes several fill-empty cycles as it travels through a plant. These are shown schematically in Figure 5. A given plant may have some or all of these cycles. Each is associated with a vapor loss due to pure displacement of the gas above the container as it fills. The amount actually lost in each step will vary as the vapor pressure varies due to temperature, solutes, and degree of saturation of the gas in the vapor space.

c. Resin Reactor Usage — The amount of resin reactor volume attributable to various types of operations is given in Table 12. A total of 371 kettles were reported by type 1 plants and 218 by type 3. The average kettle volume is considerably higher for type 3 than for type 1. This is partly due

TABLE 10

SOLVENT TANKS OVER 5,000 GALLONS
(Questionnaire Data)

	Type 1	Type 2	Type 3	Total
Number of Tanks	681	497	205	1,383
Number Uncontrolled	185	278	106	569
Turnover (MM gal/yr)	57.06	44.01	60.84	161.91

TABLE 11

FILLING LOSSES FOR SELECTED SOLVENTS @ 20°C
(Questionnaire Data)

Solvent	V.P. @ 20°C, mm	Molec. Wt.	Filling Loss, lb/100 gal
Acetone	186	58	0.494
Ethyl Acetate	74	88	0.299
Toluene	22	92	0.0927
Mineral Spirits	2 (est.)	160 (est.)	0.0147

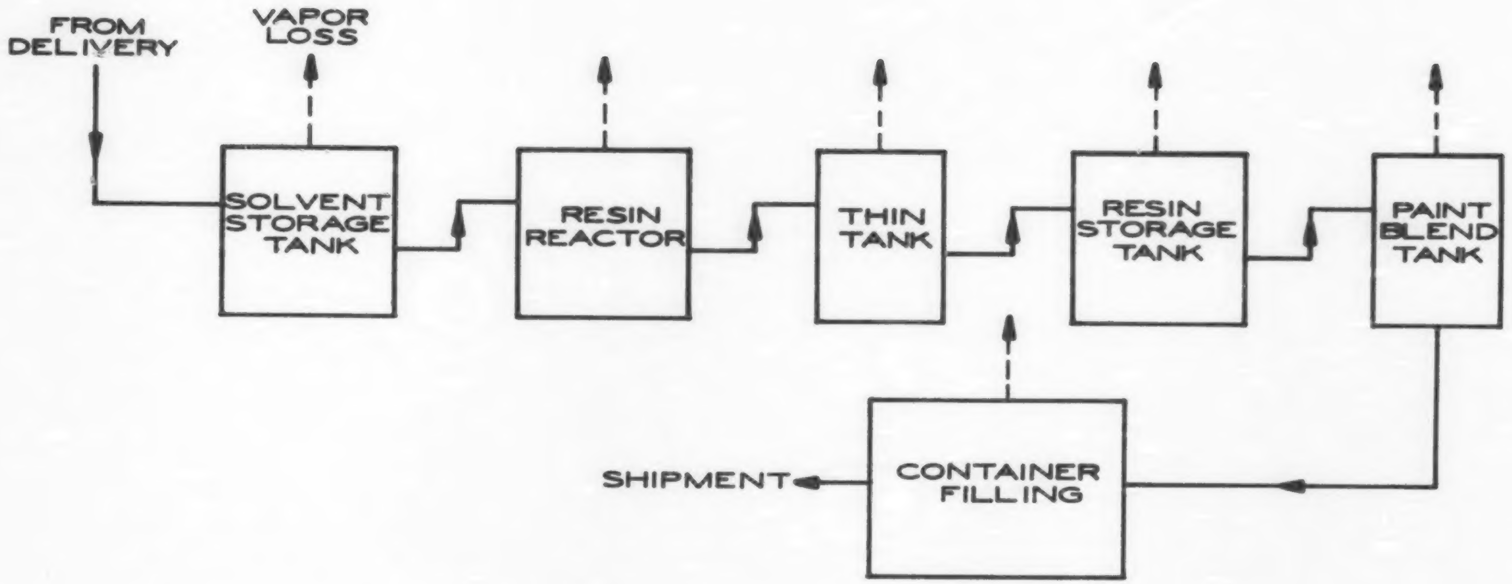


FIGURE 5

FLOW SHEET FOR SOLVENT
THROUGH A PAINT – RESIN PLANT

to the fact that type 1 plants have a large number of varnish kettles and these are generally rather small.

Table 13 gives the number of plants which operate a particular type of reactor. The alkyd kettles are divided into those which are used primarily for fusion cooking and those which are primarily for solvent processing. Examination of the data indicates that, in terms of gallons, solvent processing is strongly favored by type 1 plants while the opposite is true for type 3 plants. In terms of numbers of plants, however, the preferences are much less pronounced.

The production of water based emulsions tends to be concentrated in the type 3 plants. Varnishes, on the other hand, tend to be produced by type 1 plants. Varnishes in this context are whatever the plants responding chose to call varnishes. Most of the time they consisted of the classic oleoresinous type.

The tendency to operate on a 24 hour basis increased as the size of the resin plant increased. Two shift operation was most common in the small to medium size plants. The large producers were almost always 24 hour operations. A few of the small producers reported a single 8 to 10 hour shift.

C. Material Balance For Model Plant

One of the purposes of this industry study is to determine the financial impact of air pollution control on the paint industry. To accomplish this purpose a model plant was developed and has been used to:

1. Develop an operating statement for the uncontrolled plant.
2. Develop an operating statement for the plant using best control equipment and compare with above.
3. Develop plant balance sheet to show the effect of capital investment for air pollution control equipment upon assets, liabilities and equity.

Sherwin-Williams has been retained as the subcontractor to develop the model plant economics.

1. Design Basis

The major features for the model paint plant were based on the design contained in a paper presented by Mr. R. F. Brewster at the National Paint and Coating Association meeting on October 31, 1972.[9] This design resulted from a study by the Management Committee of the NPCA. By using this information, it was possible to take advantage of the expertise of those in the industry, as well as provide a common ground with the industry. Copies of some of the slides and calculation sheets on which the paper was based were provided by Mr. Brewster.

TABLE 12

REACTOR USAGE, GALLONS OF KETTLE VOLUME

(Questionnaire Data)

	Type 1	Type 3	Total
Alkyd			
Fusion	45,955	82,080	128,035
Solvent	143,900	47,000	190,900
Varnish	64,788	10,070	74,858
Water Emulsion	47,977	154,000	201,977
Other Resin*	116,450	243,325	359,775
Other or Unspecified**	33,325	45,820	79,145
Total	452,395	582,295	1,034,690

*Such as polyester, epoxy, solvent based acrylic, etc.

**Includes heat bodying oils.

TABLE 13

RESIN PROCESSING, NUMBER OF PLANTS

(Questionnaire Data)

	Type 1	Type 3
Total	76	39
Alkyd (Fusion and/or Solvent)	45	16
Fusion	23	10
Solvent	33	9
Varnish	34	9
Water Emulsion	20	9
Other Resin*	15	13
Other or Unspecified**	22	8

*Such as polyester, epoxy, solvent based acrylic, etc.

**Includes heat bodying oils.

The model plant developed for this study differs from the NPCA plant in two important respects: (1) a resin plant has been added to produce trade sales and industrial alkyds; and (2) the plant was modified to operate on a two-shift rather than single-shift basis. The first of these changes necessitates additional facilities for handling the resin raw material as well as space and equipment for resin production itself. The second change requires additional space for raw material and finished product storage and handling as well as increased labor requirements. The paint manufacturing equipment itself (mixers, dispersers, filling equipment, etc.) remains unchanged.

The NPCA plant was designed to produce one million gallons per year on a single-shift basis. In projecting to two shifts, one should take into account the fact that some of the ball or pebble milling processes require more than eight hours. Thus, going to two shifts will not necessarily double the output of these operations. These, however, represent a small percentage of total production. Of more importance is the question of labor efficiency. Industry personnel have indicated that the efficiency of the second shift tends to be less than that of the first shift. Efficiency drops even further if a third shift is used. Based on their comments, it will be assumed that the plant produces at 90% efficiency on the second shift. The plant, then, will produce 1,900,000 gallons per year. It is assumed that the product distribution is the same as that for the NPCA plant. This distribution, with the revised gallon production, is given in Tables 14, 15, and 16. Table 16 contains, in addition, the resin plant output, which will be discussed later.

It may be noted that the industrial coatings listed as "Other Solvent Based" were specified to include the following:

Gallons	Type
95,000	Monomer modified alkyd for fast dry coatings
95,000	Acrylic baking enamel
190,000	Alkyd urea baking enamel

In selecting these particular types, the size and expected level of technical sophistication of the model plant were taken into consideration. These resins are to be purchased from outside suppliers rather than manufactured in the plant.

2. Production and Inventory

The design of the NPCA plant is based on certain assumptions concerning production rates and inventory. For consistency, these assumptions have been retained for this study. The objective is to turn trade sales inventory six times a year and industrial inventory 18 times. That is, the average inventory levels are 16⅔% of annual trade sales shipments and 5⁵/₉% of annual

TABLE 14

MODEL PLANT

PRODUCT MIX

60% Trade	1,140,000 Gallons
70% Latex	800,000 Gallons
30% Alkyd	340,000 Gallons
40% Industrial	760,000 Gallons
50% Alkyd	380,000 Gallons
50% Other	380,000 Gallons
Total	1,900,000 Gallons

TABLE 15

MODEL PLANT

TRADE SALES COLOR DISTRIBUTION

	Latex	Alkyd	Total
Whites and tint bases	673,000	283,000	956,000
Tints (12 shades)	94,000	33,000	127,000
Solid colors (7 colors)	33,000	24,000	57,000
Total	800,000	340,000	1,140,000

TABLE 16

MODEL PLANT

PRODUCT TYPE

	Latex		Alkyd		Total	
Trade sales	%	gal	%	gal	%	gal
Outside H.P.	14.4	275,000			14.4	275,000
Outside trim			0.83	15,800	0.83	15,800
Inside flat	27.6	525,000			27.6	525,000
Inside semi-gloss			11.78	224,000	11.78	225,000
Inside gloss			5.39	100,200	5.39	100,200
Sub-total	42.0	800,000	18.00	340,000	60.00	1,140,000

Industrial sales	%	gal
Alkyd	20	380,000
Other solvent based	20	380,000
Sub-total	40	760,000

Alkyd resin	Pounds (NVM)
Long oil trade sales	1,025,000
Medium oil industrial	285,000
Short oil industrial	856,000
Total	2,166,000

industrial shipments. It is further assumed that production rates are held uniform throughout the year. Shipments of trade sales products will fluctuate through the year as shown in Figure 6. Industrial shipments are uniform.

The consequences of these assumptions are that trade sales inventory must successively increase and decrease to accommodate the annual sales curve. The typical trade sales inventory curve for this plant is shown in Figure 7. Inventory peaks at 29% of annual sales in March and declines to a low of 5% of annual sales in September. The finished goods inventory, including its distribution by type of container, is shown in Table 17. Annual production and maximum inventory levels by various categories are presented in this table. The distribution is as given for the NPCA plant, whereas the actual numbers have been revised upwards to account for the increased yearly production assumed for the present plant.

These assumptions may be somewhat unrealistic in some respects. First, the uniform production rate may not be representative of the way many plants operate. Second, the minimum trade sales inventory of 5% of annual shipments may be somewhat low. Both these points were discussed in the NPCA report and it was felt by the authors that the plant, nonetheless, provided a useful base from which to relate other situations.

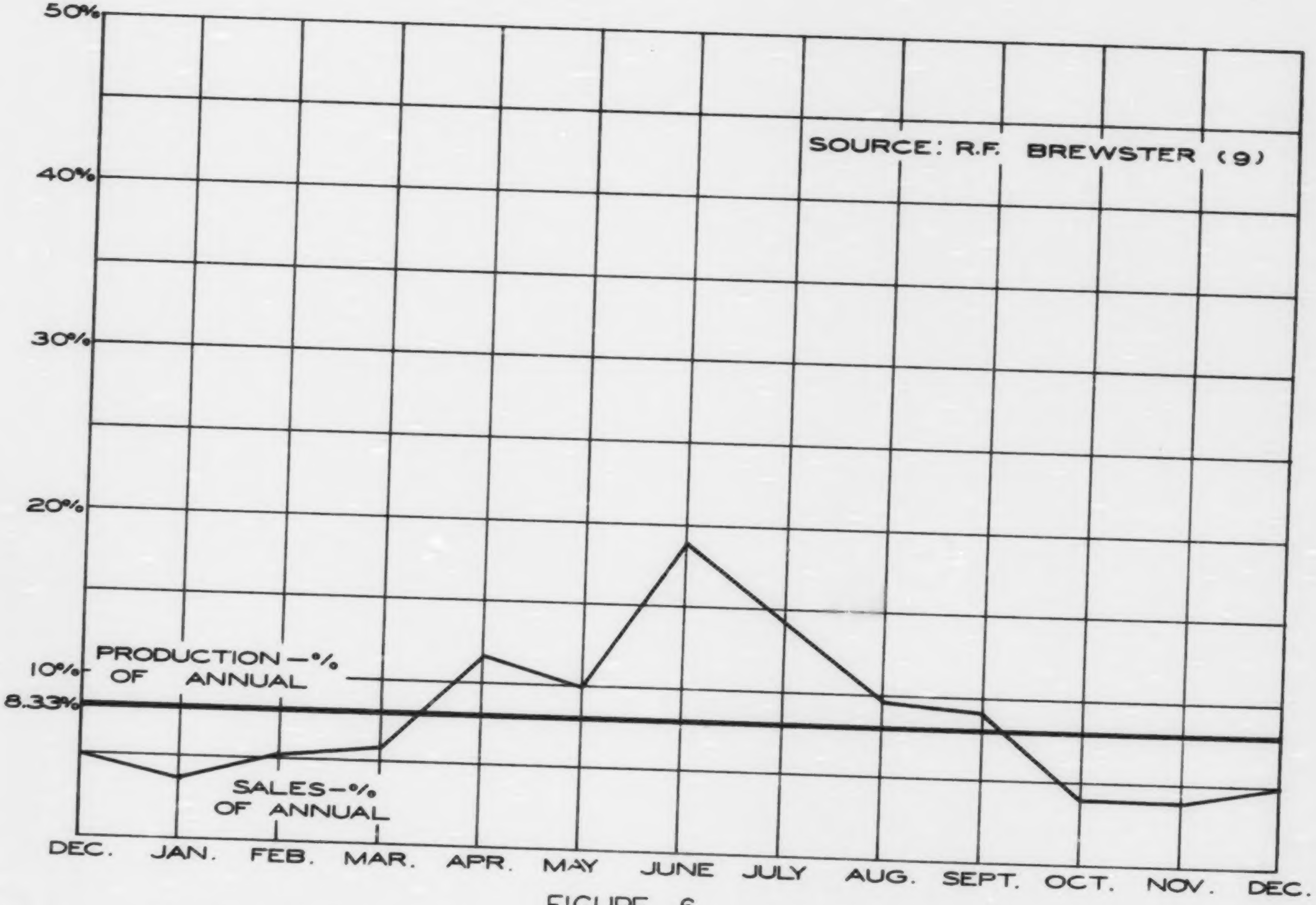
3. Equipment Requirement

a. Paint Plant — Equipment requirements worked out for the NPCA plant are unchanged for this study. The product distribution is the same, while increased production is accomplished solely by the addition of another working shift. The equipment summary is presented in Table 18.

It is anticipated that high speed dispersion will be suitable for almost all the latex paints, as well as for a relatively large portion of the architectural solvent finishes. The sand mills will process those items having an intermediate difficulty of dispersion. The output of the sand mills is assumed to be at an hourly rate five to ten times the size designation. Neither the high speed dispersers nor the sand mills reduce particle size (i.e. grind).

The pebble mills will be used primarily for bright colored industrial finishes and for certain trade sales products. Ball mills will see relatively limited use — primarily hard to disperse dark colors.

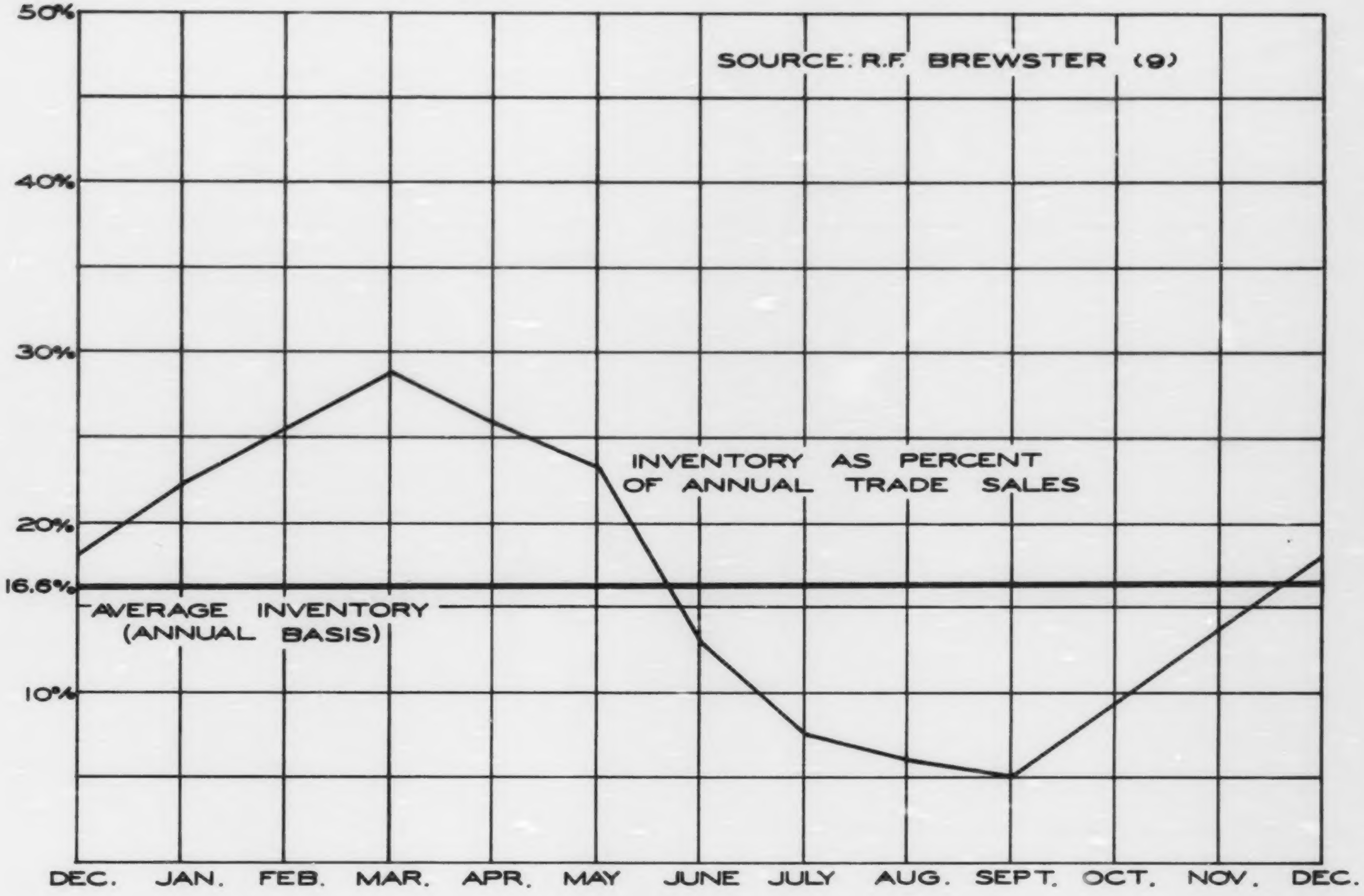
The ball and pebble mills were selected to provide a continuous capacity range rather than to provide a given output. Mills of this type are assumed to have an effective working capacity of 20% to 50% of actual capacity. Outside this range, they do not operate properly. Figure 8 illustrates, on a logarithmic scale, the grinding capacities of the ball and pebble mills. Since the scale is logarithmic, each mill is represented by a bar of equal length. This chart portrays the degree of overlap



SOURCE: R.F. BREWSTER (9)

FIGURE 6

TYPICAL SALES AND PRODUCTION CURVES — TRADE SALES PRODUCTS



SOURCE: R.F. BREWSTER (9)

FIGURE 7

TYPICAL INVENTORY CURVE —— TRADE SALES PRODUCTS

TABLE 17

MODEL PLANT

FINISHED GOODS INVENTORY — MAXIMUM PROJECTION

	Annual		Maximum Inventory	
	Production (gal)	Packages (number)	Gallons	Number
Trade				
Gallons	1,140,000		330,000	
Drums		0		0
5		22,800		6,600
1		912,000		264,000
1/4		420,000		119,000
1/8		91,200		26,400
Industrial				
Gallons	760,000		42,000	
Drums		10,400		575
5		38,000		2,110
Total				
Gallons	1,900,000		372,200	
Drums		10,400		575
5		60,800		8,710
1		912,000		264,000
1/4		420,000		119,000
1/8		91,200		26,400

TABLE 18
MODEL PLANT
EQUIPMENT SPECIFICATIONS

Pebble mills	Diameter	Length	Total gallons
1	21 in.	28 in.	28.5
1	24 in.	36 in.	52
1	32 in.	36 in.	94
1	42 in.	48 in.	216
1	60 in.	72 in.	699
1	72 in.	96 in.	1404
Ball mills			
1	32 in.	32 in.	125
1	48 in.	60 in.	470
Sand mills			
1			3
1			8
1			16

High speed dispersers

2 – 10 H.P.
1 – 25 H.P.
1 – 50 H.P.
1 – 100 H.P.

Mixing tanks	Number	Size, gallons
	20	220, portable
	14	550
	8	1,100
	4	2,200

Twin fillers	"Instantaneous" rate
2	24 one-gallon/min
	40 quarts/min
	60 pints/min

Associated filling equipment

1 – Labeller
1 – Bail-O-Matic
1 – Packing Station
1 – Case Sealer

Filtering equipment

1 – Two cartridge
3 – Six cartridge
2 – Vibratory screens

which exists between successive pebble mills. In this way, a continuous pebble milling capacity ranging from 5.7 to 702 gallons is obtainable.

Mixing and finishing tanks are of two types, fixed and portable. The 220 gallon portable tanks are to be used in conjunction with the high speed dispersers. The larger sizes are floor mounted and equipped with belt driven turbine drives and electric motors.

Two twin filler machines are provided. A single unit operating at an 80% utilization rate can theoretically handle all the filling operations, but it was felt that this represented a too narrow safety factor. The filling machines can be moved back and forth under the tanks.

b. Resin Plant — Since the NPCA plant did not include resin production facilities, it was necessary to start from scratch in designing this part. It was necessary to first estimate the amount of alkyd resin required. The size of the resin plant and, finally, the specific equipment required were then determined.

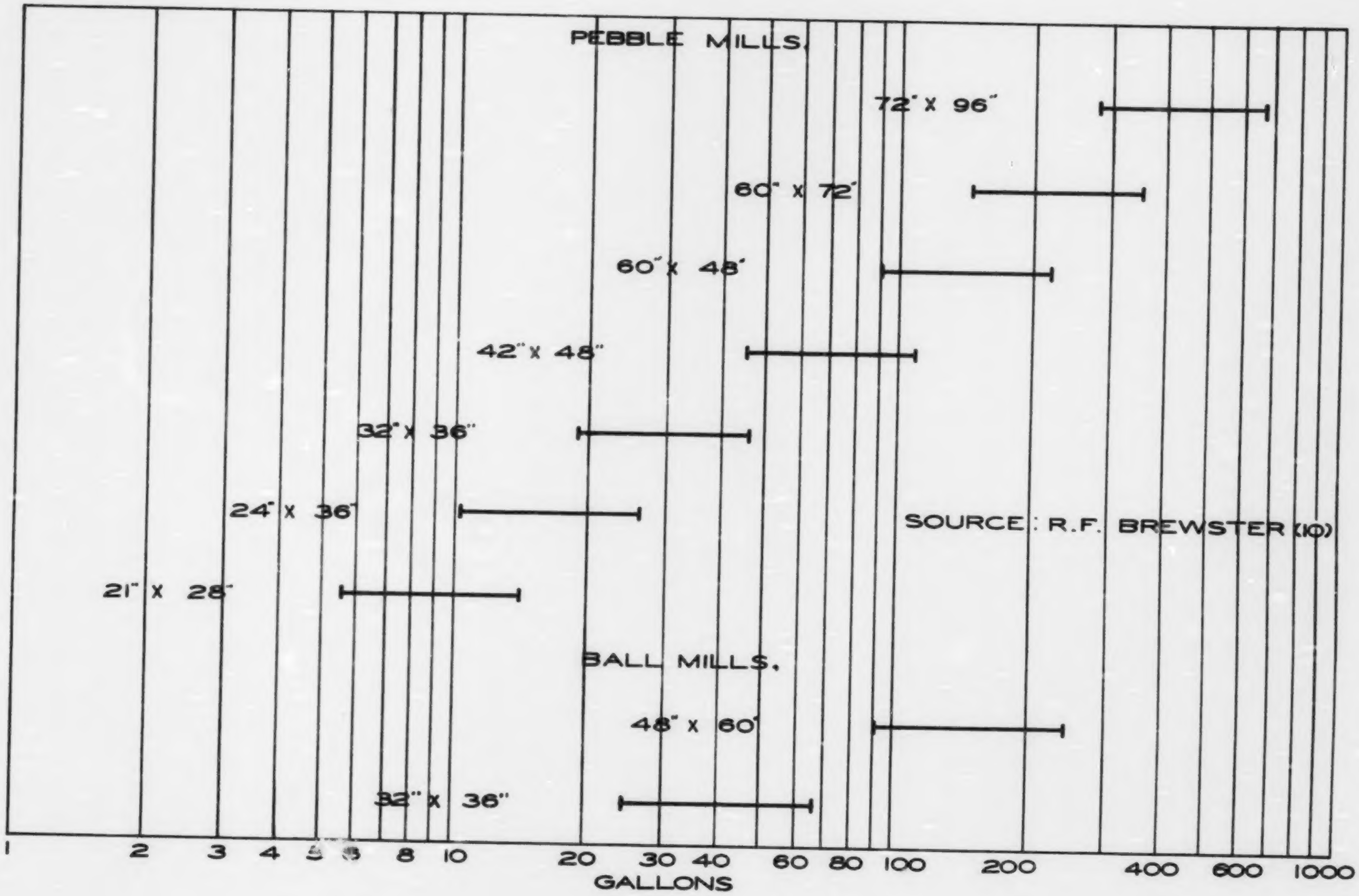
It has been assumed that the plant will produce all of its own alkyd resins. It will further be assumed that one-half of the industrial output consists of alkyd based coatings. For the NPCA plant, this means that 180,000 (trade) + 1/2 × 400,000 (industrial) or 380,000 gallons of alkyd based paints will be produced. Scaling up to two shifts, we get 1.9 × 380,000 = 722,000 gallons.

Several workable, up-to-date, paint formulations for alkyd type coatings have been supplied by Ashland Chemical Company. Based on these formulations (two of which are given in Table 19) an average resin content of about three pounds solids per gallon of paint is representative for the type of products this plant would produce. The required alkyd production is 3 × 722,000 = 2,166,000 pounds of resin solids per year.

The size of the resin reactors required for this amount of production was determined by reference to material presented earlier. As discussed in Section A-2 of Chapter 1, industry practice suggests that a medium size alkyd kettle produces about 5,000 pounds of resin solids per batch per 1,000 gallons of reactor volume.

Even if the resin plant is operated on a two shift basis, only a single batch can normally be processed per day due to the cooking times (8 to 16 hours) required. Assuming 250 working days per year, 1,730 gallons of kettle volume are required as a minimum to produce the necessary resin for the model plant.

In determining the exact configuration of the resin plant, three aspects were kept in mind; efficiency, flexibility, and cooking times. In order to obtain the efficiency of large batches and still retain the flexibility to handle a broad product line, it was decided that two reactors be installed. A



SOURCE: R.F. BREWSTER (10)

FIGURE 8

GRINDING CAPACITY – BALL AND PEBBLE MILLS

TABLE 19

MODEL PLANT

PAINT FORMULATIONS FOR ALKYD TYPE COATINGS

"Exempt" Air Dry Gloss Interior-Exterior Architectural Enamel

	lb	gal
Rutile titanium dioxide[1]	306.75	8.99
Suspension and sag control agent[2]	5.11	0.35
Loss of dry inhibitor[3]	6.13	0.56
6% Calcium naphthenate	3.27	0.42
Long soya alkyd solution (70% NVM)[4]	221.90	27.70
"Exempt" mineral spirits	73.62	11.25
Disperse to 7+ Grind (Hegman)-Cowles or Pebble Mill		
Long soya alkyd solution (70% NVM in "exempt" mineral spirits)[4]	327.20	40.90
6% Cobalt naphthenate drier	3.07	0.39
6% Zirconium drier	10.22	1.43
Anti-skinning agent[5]	1.02	0.14
"Exempt" mineral spirits	51.12	7.87
	1,009.41	100.00

[1] Titanox® 2060 Titanium Pigments Div. N.L. Industries; or equal

[2] Bentone® 38 Chemical Div. N.L. Industries; or equal

[3] LFD™ Mooney Chemicals; or equal

[4] Aroplaz® 1266-M-70 Ashland Chemical Co.: or equal

[5] Exkin No. 2™ Tenneco; or equal

TABLE 19 (continued)

Air Dry Lead Free Yellow Enamel (Industrial)

	lb	gal
Organic Yellow[1]	56.40	4.78
(Short tall oil fatty acids alkyd-50% NVM in xylol)	141.00	16.99
VM&P Naphtha	69.30	10.72
Toluene/VM&P 1/1 blend	100.00	14.58
Grind 24 hours porox balls		
(Short tall oil fatty acids alkyd-50% NVM in xylol)	313.00	37.71
Butanol	32.60	4.82
Toluene	44.00	6.08
6% Cobalt octoate drier	1.52	0.21
6% Calcium naphthenate drier	30.63	3.94
6% Manganese naphthenate drier	0.76	0.11
Anti-skinning agent[2]	0.51	0.06
	795.39	100.00

[1] DuPont's Dalamar YT-808D; or equal

[2] Exkin #2 Tenneco; or equal

degree of excess capacity was built in to compensate for equipment malfunctions, etc. and to allow increased production over and above the minimum without incorporating a third working shift.

In order to insure that all formulations can be processed in two working shifts, the largest kettle should be less than 2,000 gallons in size. Data from the questionnaire sample indicates that, as expected, process times tend to increase with the size of the batch. Up to 1,500 gallons kettle size, processing times were almost always less than 16 hours. For the larger kettles, times in excess of 16 hours were sometimes reported.

In view of these considerations, two reactors were specified. Their capacities are 1,500 gallons and 500 gallons, respectively. In summary, the resin plant description is as follows:

1. 1,500 Gallon Reactor — A reactor system similar to that shown in Figure 9 will be provided. This system can be operated as either a fusion reactor or as a solvent process reactor.

Material:	Stainless Steel
Heat Source:	Dowtherm* (Typical)
Thin Tank:	3,000 Gallons Capacity

2. 500 Gallon Reactor — Also similar to Figure 9 except that the condensers and decanter-receiver are omitted. This system operates only as a fusion reactor. The material of construction and heat source are the same as for the larger reactor. The thin tank is 1,000 gallons capacity.

c. Tankage Requirements — Tankage requirements are based on the assumption that the plant should maintain a minimum of one month's supply of raw materials. It was further assumed that liquid raw materials would be delivered in 5,000 gallon quantities. The tank volume necessary to maintain a minimum inventory of 30 days' supply can be calculated, then, by dividing the annual requirements by twelve and adding 5,000 gallons to the result. For instance, 216,000 gallons per year of odorless mineral spirits are required. The tank required is $216{,}000 \div 12 + 5{,}000 = 18{,}000 + 5{,}000 = 23{,}000$. A summary of the tankage requirements (sometimes rounded off to a convenient size) is presented in Table 20. Industry sources have suggested that while this total tankage ought to be adequate, in practice it would probably consist of a larger number of smaller tanks.

4. Raw Materials

Raw material requirements were determined by simply scaling up the NPCA raw materials sheet by a factor of 1.9 where appropriate. Additions and modifications have been made to accommodate the resin production. These changes and additions occur in the solvents, miscellaneous industrial resins, oil, glycerine, and phthalic anhydride. The latter three quantities were not present

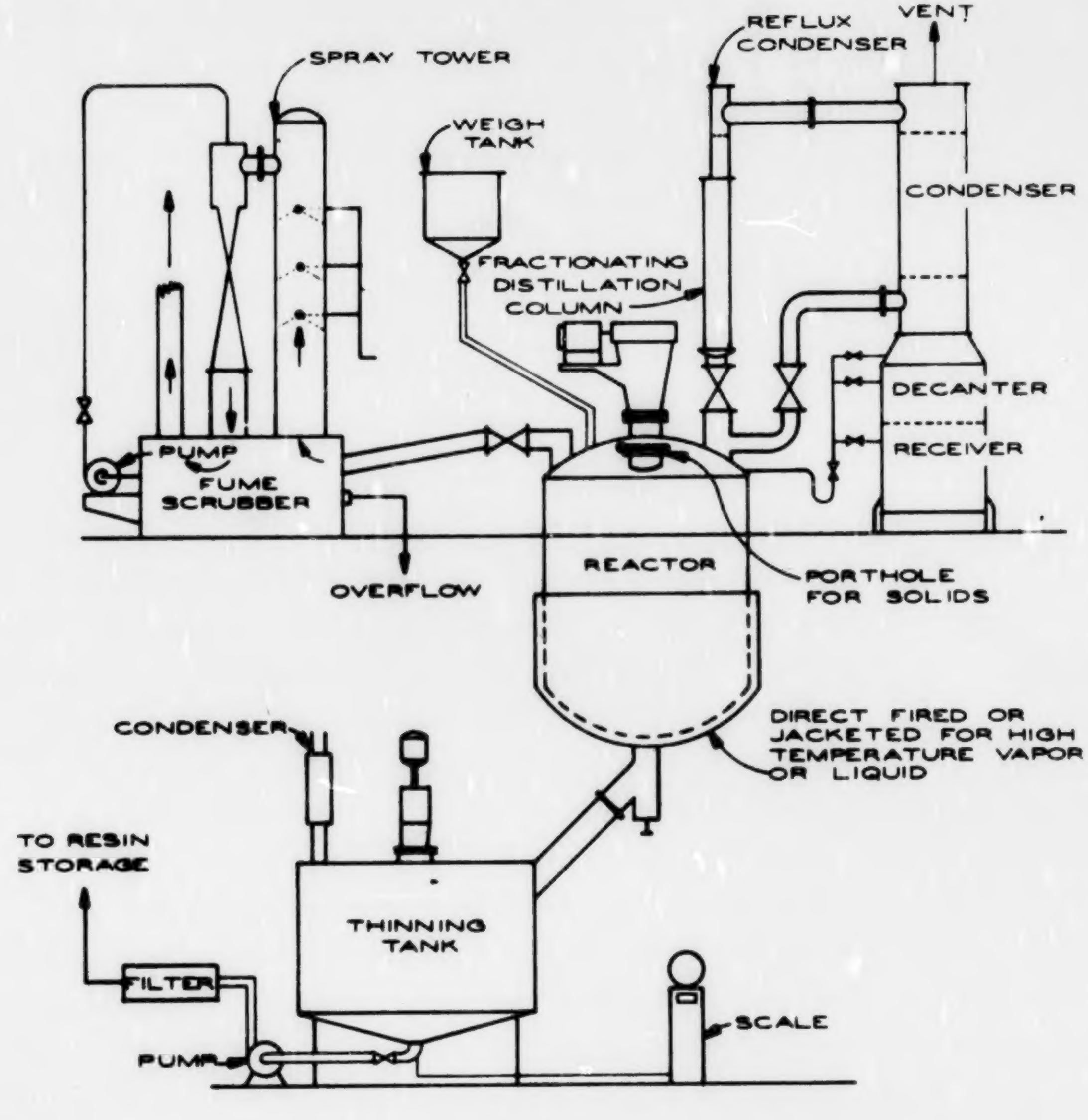


FIGURE 9
MODERN RESIN PRODUCTION SYSTEM

TABLE 20

MODEL PLANT

SUMMARY OF TANKAGE REQUIREMENTS

Size (gallons)	Contents	Location
25,000	OMS	Outside
25,000	Xylene	Outside
12,500	Oil	Inside, lower level
12,500	Oil	Inside, lower level
7,500	Glycerine	Inside, lower level
17,500	Exterior latex	Inside, lower level
22,500	Interior latex	Inside, lower level
10,000	Trade alkyd	Inside, lower level
5,000	Trade alkyd	Inside, lower level
10,000	Industrial alkyd resin	Inside, lower level
7,500	Industrial alkyd resin	Inside, lower level
1,000	Industrial alkyd	Inside, lower level
1,000	Industrial alkyd	Inside, lower level
1,000	Industrial alkyd	Inside, lower level
1,000	Industrial alkyd	Inside, lower level
1,000	Waste solvent	Outside
1,000	Waste solvent	Outside
1,000	Aqueous waste	Inside, lower level

at all in the NPCA plant.

The raw materials requirements for resin production are based on the following assumptions:

1. Trade sales alkyds consist of long oil types at an average of 65% oil.
2. 1/4 of the industrial alkyds are medium oil at an average of 50% oil.
3. 3/4 of the industrial alkyds are short oil types at an average of 40% oil.

A weighted average can be calculated as follows:

1.8/3.8 × 0.65 = 0.308

0.5/3.8 × 0.50 = 0.066

1.5/3.8 × 0.40 = 0.158

The average alkyd contains 53% oil. Assume also that, on the average, PA and glycerol are present in a 2:1 weight ratio. This represents an excess hydroxy content (based on PA and glycerine only) of about 20%. Resin raw materials can be calculated as follows:

Basis 1,140,000 pounds resin solids (one shift):

1,140,000 × 0.53 = 616,000 pounds oil

Correction for 5% loss (mostly water): 1.05 × 1,140,000 = 1,200,000 pounds

Glycerol + PA = 1,200,000 − 616,000 = 584,000 pounds.

Glycerol: 584,000 × 1/3 = 195,000 pounds

PA: 584,000 × 2/3 = 390,000 pounds

For two shift operation, assuming 90% efficiency on the second shift, the approximate requirements are:

1,170,000 pounds oil

370,000 pounds glycerine

740,000 pounds PA

By volume the liquid requirements are:

1,170,000/7.64 = 153,000 gallons oil (as Soya)

370,000/10.5 = 35,000 gallons glycerine

In addition to these materials, solvent requirements over and above those in the NPCA plant must be met. Since the alkyds are to be produced in the plant, the solvent that otherwise would have been a part of the purchased resin solution must be supplied separately. For the trade sales alkyds, this solvent will be an odorless mineral spirit. The industrial alkyds will require a stronger solvent such as xylene or an equivalent exempt solvent system. These solvent requirements have been incorporated in the raw materials data sheet which is given in Table 21. This is followed by Table 22 which lists packaging material requirements. These tables contain some revised entries prepared by Sherwin-Williams based on the NPCA report and on the resin requirement outlined earlier.

5. Labor Requirements

In revising and expanding the NPCA manning chart, the following assumptions were made:

1. The numbers and types of personnel in the factory and filling areas are the same for the second shift as for the first shift.
2. All shipping and receiving is done on the first shift.
3. The resin plant requires two men on each shift.
4. Shipping and receiving personnel need to be increased by 50% to handle the increased capacity.

These and other changes have been incorporated into the revised manpower requirements shown in Table 23. A manning chart for the plant is given in Figure 10.

6. Plant Layout and Flow Sheet

A flow sheet for the plant is given in Figure 11. Prints of the plant layout incorporating the design changes necessary to accommodate the resin plant and increased capacity are presented in Figures 12 and 13. In order to operate under the same storage and inventory assumptions as the NPCA plant, it will be necessary to nearly double warehouse, raw material storage, and shipping and receiving areas. This is in addition to any plant expansion needed to accommodate the resin production facilities. The manufacturing and filling areas are essentially unchanged from the NPCA plant. A site plan is given in Figure 14.

II. EMISSIONS

There are two major types of emissions from a paint plant. These are confined (or non-fugitive) and fugitive. Non-fugitive emissions are those that are collected by and confined within an exhaust system with or without an air pollution control device. Fugitive emissions are those that escape into the plant atmosphere from various operations and exit the plant buildings through the doors and windows in an unregulated fashion.

A. Description of Emissions

These two types of emissions can both be further subdivided into gaseous and particulate emissions. Details of each type of fugitive and non-fugitive emissions are discussed on the following page.

TABLE 21

MODEL PLANT

ANNUAL RAW MATERIAL CONSUMPTION (FINISHED OUTPUT OF 1.9 MILLION GALLONS)

Raw Material	Trade Sales		Industrial Finishes	
	Pounds	Gallons	Pounds	Gallons
Pigments & Extenders				
Titanium Dioxide	2,039,000		760,000	
Misc. Colors	27,500		380,000	
Silica	1,179,000		232,750	
Calcium Carbonate	893,500		– –	
Talc	475,850		522,500	
Clay	199,700		– –	
Resins – Manufactured				
Soya Oil	714,000		492,000	
Phthalic Anhydride	276,000		470,000	
Glycerine	138,000		247,000	
Resins – Purchased				
Exterior Latex (11.42 lb/gal)	1,644,500		– –	
Interior Latex (10.6 lb/gal)	2,141,200		– –	
Aropol 830-V-60	– –		400,000	
Aroplaz 7435-XM-50*	– –		870,000	
Resimene V-920*	– –		152,000	
Acryloid AT-5 1*	– –		510,000	
Epon 1001X75*	– –		60,600	
Solvents & Miscellaneous				
Driers (9.8 lb/gal)	55,890		81,340	
Misc. Solids	29,200		– –	
Misc. Liquids (8 lb/gal)	241,600		30,400	
Water		272,300		– –
Odorless Mineral Spirits		169,500		– –
Anti-Skin (7.72 lb/gal)	26,402		22,774	
Toluene		– –		45,600
Xylene		– –		221,400
Aromatic 100 (Solvesso 100)		– –		20,900
Aromatic 150 (Solvesso 150)		– –		6,975
VM + P Naphtha		– –		32,650
Butanol (6.74 lb/gal)	– –		20,894	
Cellosolve* Acetate	– –		67,300	
Triethyl Amine (6.07 lb/gal)	– –		577	

TABLE 22

MODEL PLANT

ANNUAL PACKAGE & PACKAGE MATERIAL REQUIREMENTS (FINISHED OUTPUT OF 1.9 MILLION GALLONS)

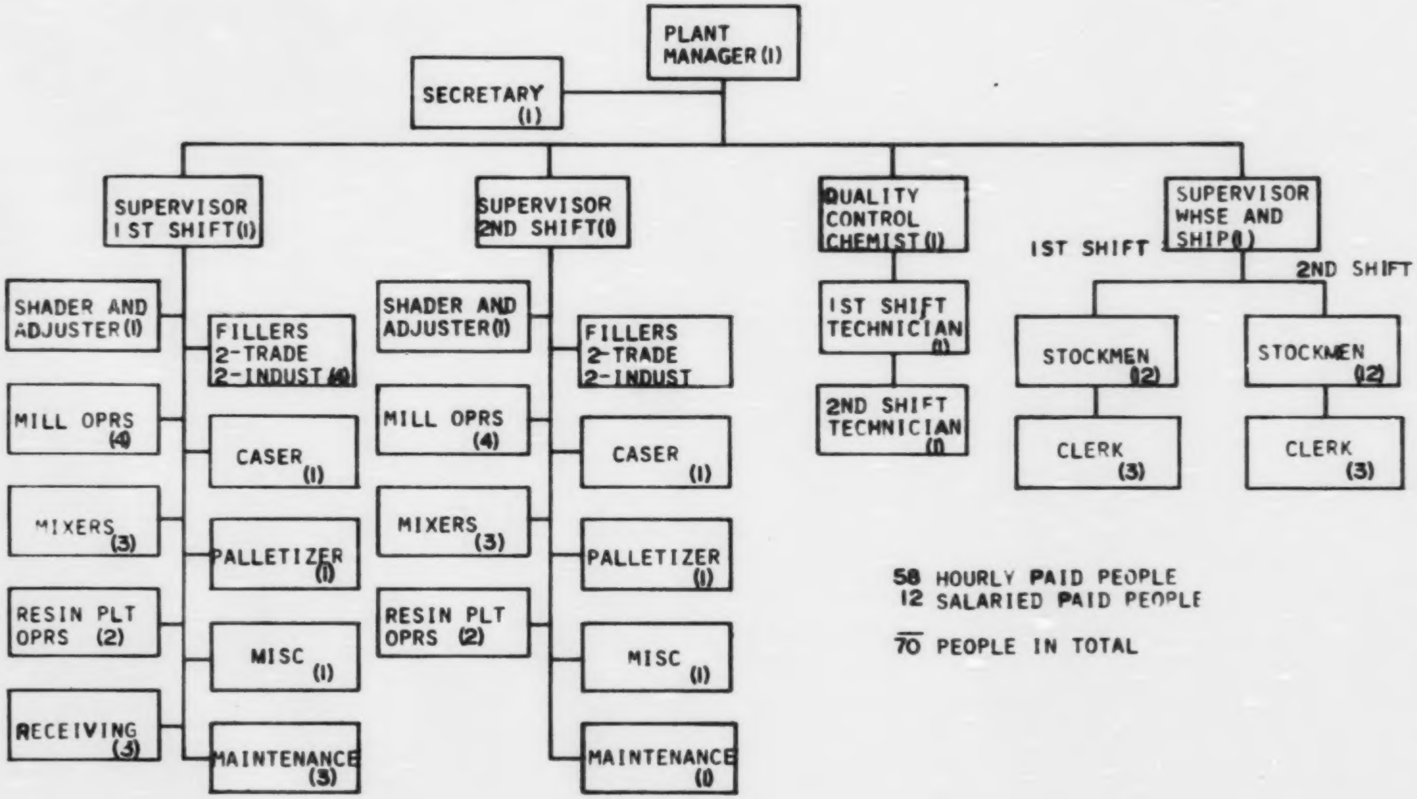
Package Type	Trade Sales Quantity	Industrial Sales Quantity
Packages		
Drums (55 gal)	– –	10,364
Pails (5 gal)	22,800	12,350
Pails (5 gal) (Interior Coated)	– –	25,650
Cans (gal)	273,600	– –
Cans (gal) (Interior Coated)	638,400	– –
Cans (qts)	205,200	– –
Cans (qts) (Interior Coated)	205,200	– –
Cans (pts)	91,200	– –
Labels		
5 gallon size	22,800	38,000
Gallon size	912,000	– –
Quart size	410,400	– –
Pint size	91,200	– –
Cartons		
Gallon size (4 gals)	228,000	– –
Quart size (6 qts)	68,400	– –
Pint size (12 pts)	7,600	– –
Pallets (30" x 42" Size)		
Drums	– –	5,182
5 gal pails	1,425	2,375
Gallons	9,500	– –
Quarts	977	– –
Pints	136	– –

TABLE 23

MODEL PLANT

LABOR REQUIREMENTS

No. People	Job Title
Salaried	
1	Plant Manager
1	Secretary
1	Supervisor 1st Shift
1	Supervisor 2nd Shift
1	Supervisor Warehouse & Shipping
1	Quality Control Chemist
2	Quality Control Technician
3	Clerks 1st Shift
1	Clerk 2nd Shift
Hourly Paid Employees	
1st Shift Workers	
15	Various Classifications
2	Resin Plant Operators
2	Fillers — Industrial
2	Fillers — Trade
2	Caser & Palletizer
12	Stockman
2nd Shift Workers	
10	Various Classifications
2	Resin Plant Operators
2	Fillers — Industrial
2	Fillers — Trade
2	Caser & Palletizer
5	Stockman



58 HOURLY PAID PEOPLE
12 SALARIED PAID PEOPLE

70 PEOPLE IN TOTAL

FIGURE 10

MODEL PLANT
FACTORY MANNING CHART
(FINISHED OUTPUT 1.9 MILLION GALLONS)

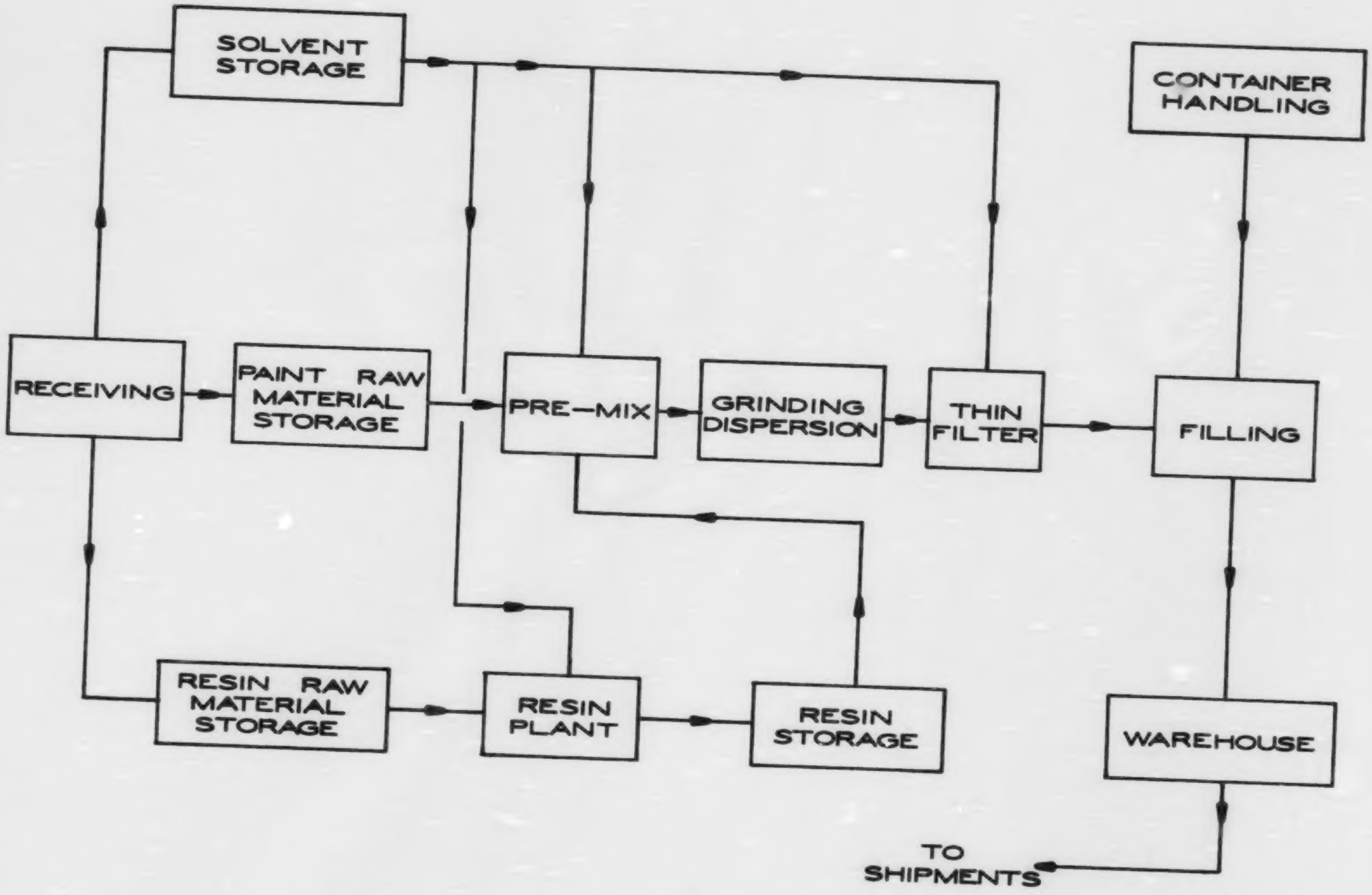


FIGURE II

MATERIALS FLOW SHEET
FOR MODEL PAINT PLANT

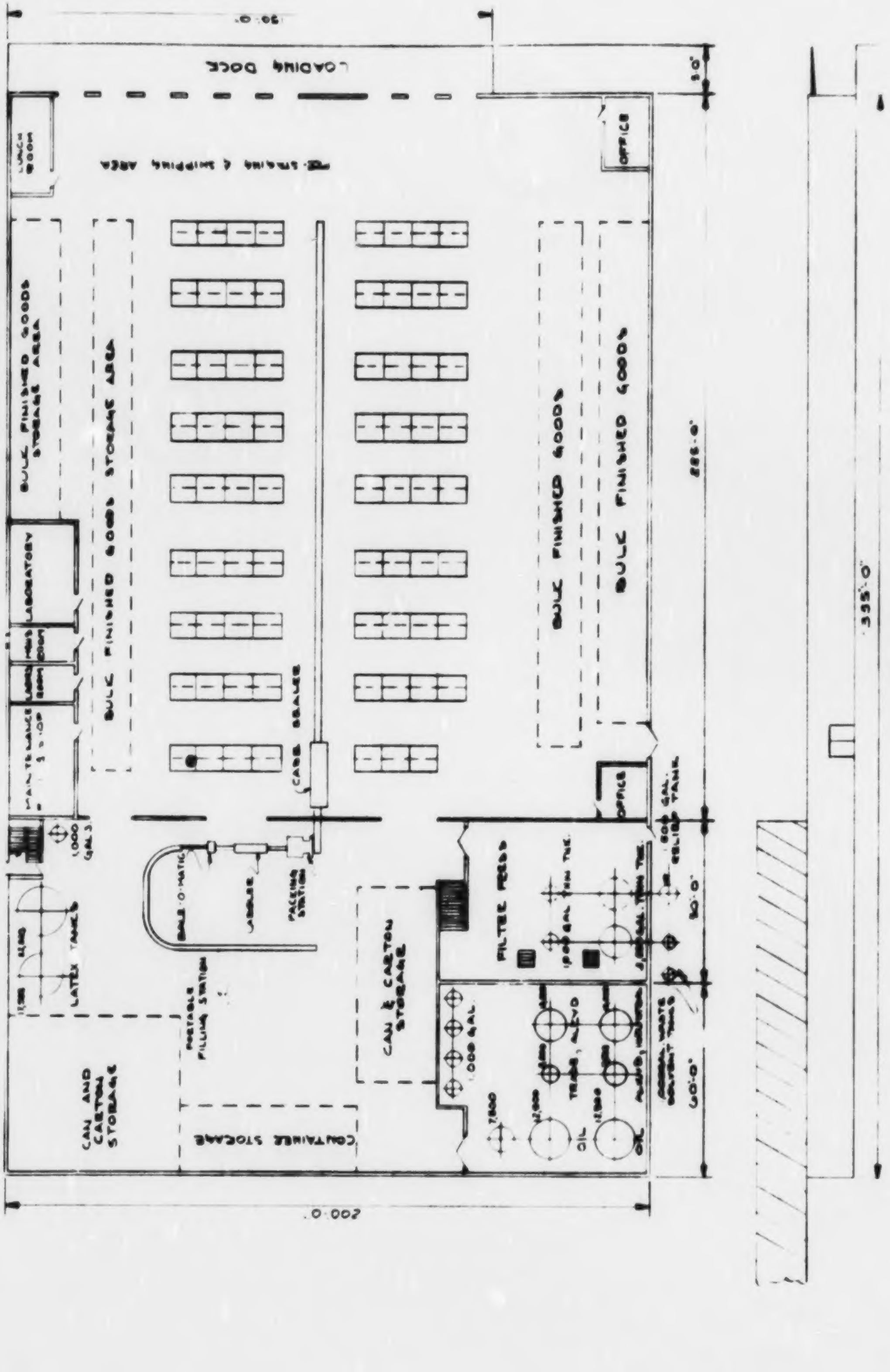


FIGURE 12
MODEL PAINT PLANT
(LOWER LEVEL)

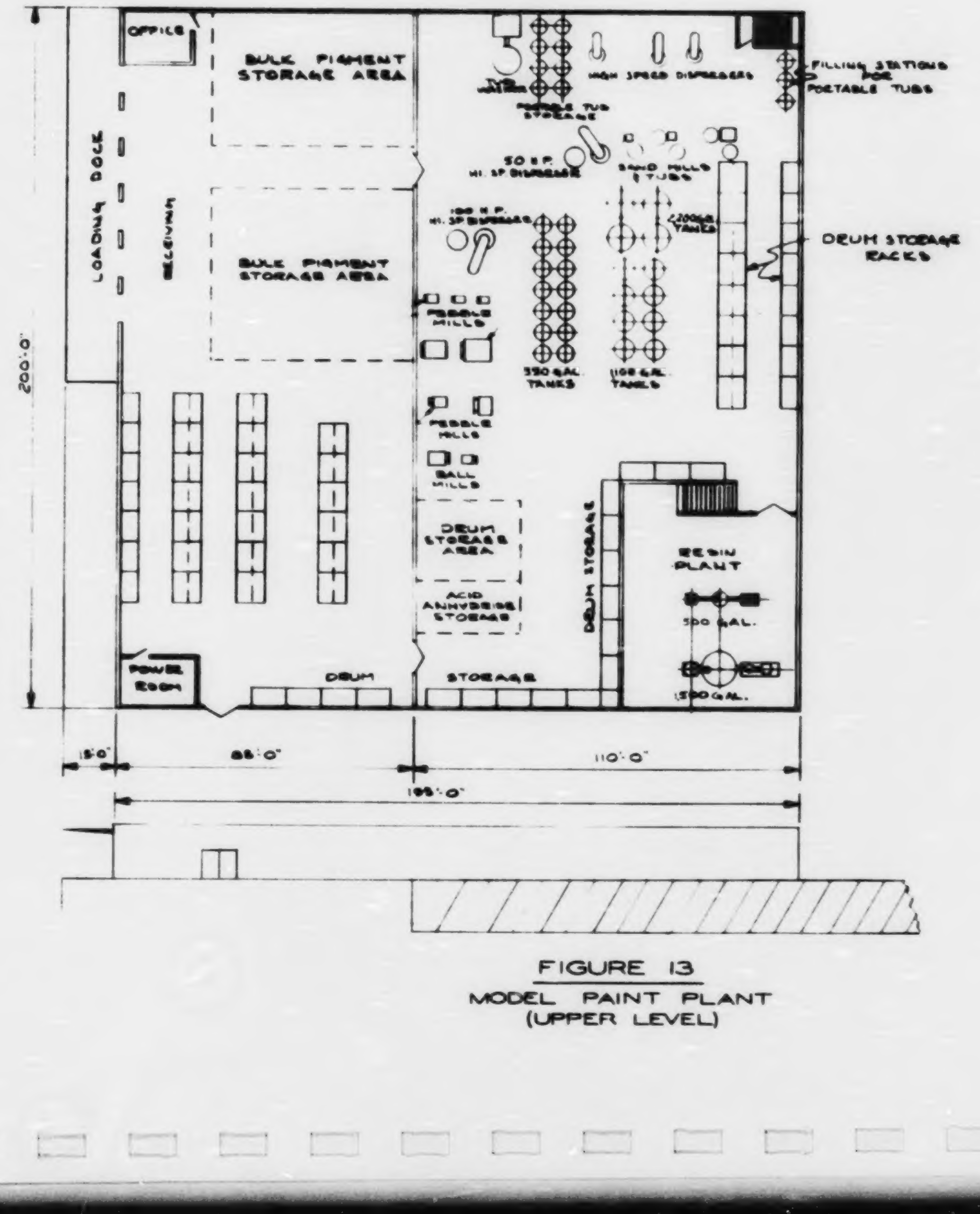


FIGURE 13
MODEL PAINT PLANT
(UPPER LEVEL)

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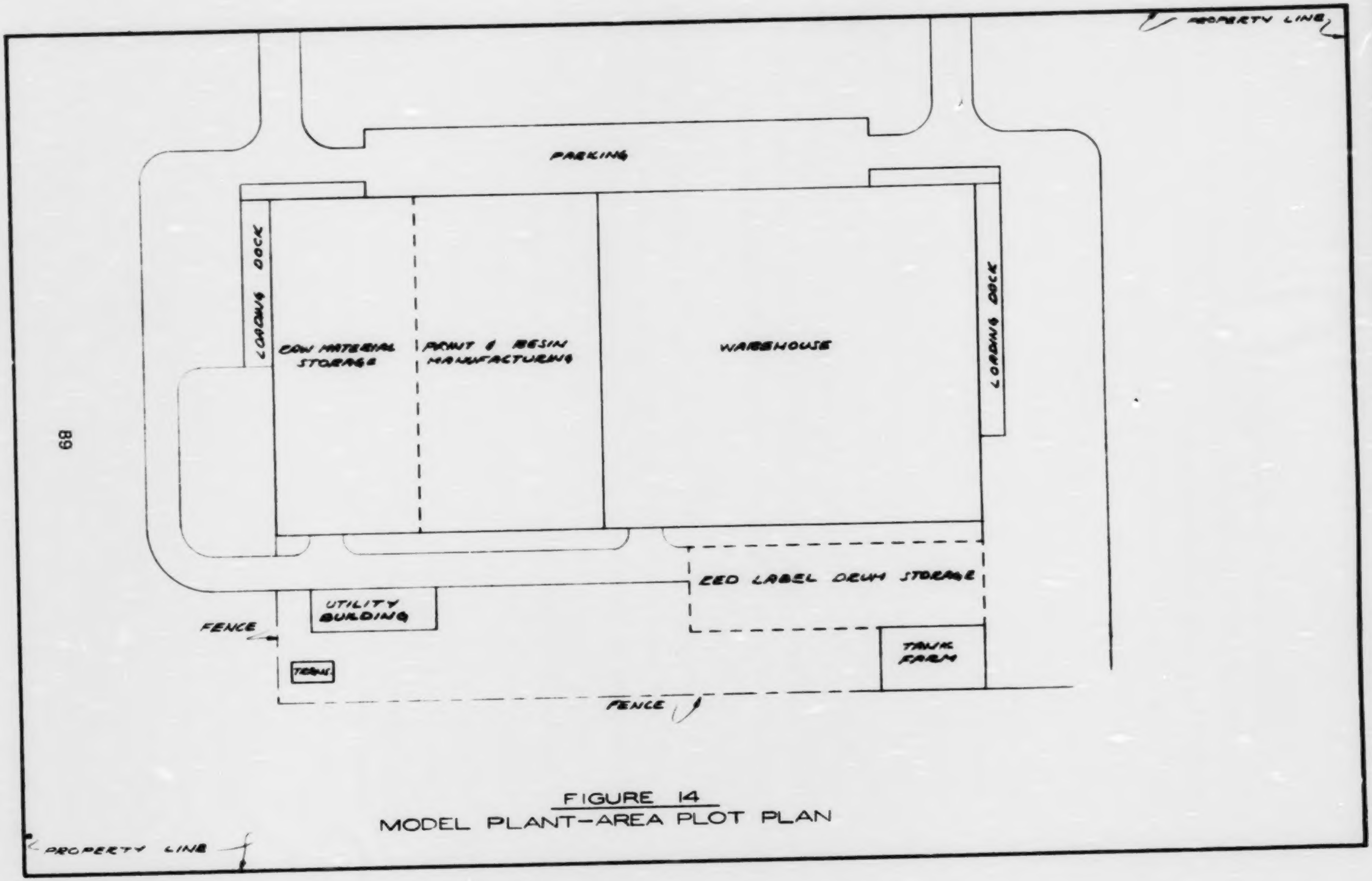

FIGURE 14
MODEL PLANT-AREA PLOT PLAN

1. Fugitive — In today's typical paint plant there are two types of fugitive emissions. These are pigment particulate and paint solvents. In a small percentage of the plants an attempt is made to collect these emissions. The incentive for doing so is based on insurance requirements as well as occupational, health and safety rather than for air pollution considerations or regulations. The newly passed Occupational Safety and Health Act (OSHA) will have a dramatic effect on the paint industry practice and necessitate the collection of fugitive emissions in the future.

Fugitive particulate emissions consist primarily of the various dry material used such as pigments and extender. Details of these pigments are discussed in Chapter 8 of this report. As a general rule, the pigments are received and stored in 25 to 50 pound paper sacks or fiber drums. Modern pigment manufacturers have developed finely sized pigments, 0.05 to 0.25 microns, for ease of dispersion into the paint vehicle. Loading of these fine pigments into grinding equipment results in fugitive particulate dust emissions into the surrounding plant areas. This dust is either collected by a ventilation and exhaust system or allowed to settle and later collected as part of the general housekeeping requirements. The pigment particles tend to agglomerate during shipment and storage and the losses during loading are not as significant as might be associated with this submicron particle size.

A variety of resins are received as granular or flaked solids which are of large size and do not result in a fugitive dust emission. The manufacturer of these solid resins, however, does encounter fugitive emission problems in his flaking or grinding operations.

Solvent emissions occur in almost every phase of paint and varnish manufacturing and in numerous locations throughout individual plants. A listing of emission points is given below:

	Location	Operation	Temperature	Pressure, Atm
a.	Resin Plant	Thinning	200 to 300°F	1
b.	Resin Plant	Filtering	200 to 300°F	1
c.	Resin Plant	Storage Tanks	100°F	1
d.	Paint Plant	Blending Tanks	Ambient	1
e.	Paint Plant	Grinding	Ambient	1
f.	Paint Plant	Dispersion	Ambient	1
g.	Paint Plant	Holding Tank	Ambient	1
h.	Paint Plant	Filtering	Ambient	1
i.	Paint Plant	Packaging	Ambient	1
j.	Paint Plant	Storage Tanks	Ambient	1

The extent of these emissions vary with the type of operation and the effort extended to control atmospheric losses. The high temperature thinning and filtering results in the largest emissions, while packaging in drums and cans contribute the smallest emission. Other operations contribute intermediate emissions which vary depending on the degree of control exercised and the vapor pressure of the solvent used. Simple good housekeeping rules, such as keeping loading hatches closed, will significantly reduce these emissions.

In some cases, efforts are made to collect fugitive emissions by use of local exhaust systems. More frequently, however, they are exhausted from the building by general building exhaust fans which ventilate areas having the highest contaminant concentration.

The total quantities of solvent losses as fugitive emissions have not been extensively measured to date and are not well-known. As a percentage of the total solvent used, these losses are relatively small. As a percentage of total solvent loss, they are quite significant. Details are presented in Part D of this Section.

The quantities of fugitive pigment emissions are also not well-known but represent a very small percentage of the total pigments used in paint manufacturing. The quantity of emissions cannot be easily measured directly but can be estimated using weight balance calculations on plants with an efficient particulate collection system. This system will be described in more detail in Chapter 5.

2. Non-fugitive — The number of regulated emissions emanating from a paint plant will vary significantly with the type of operation involved. Some trade sales plants that manufacture none of their own resins and make no effort to confine solvent losses during dispersion, filtering, or storage, will have no non-fugitive emissions. On the other hand, resin plants or paint plants producing resins and varnishes are likely to have a number of non-fugitive emissions. These emissions consist primarily of organic vapors in air or inert gas streams.

3. Chemical and Physical Properties — There are two significant types of organic vapors generated in paint manufacturing. These are varnish and resin kettle emissions which usually fall into the non-fugitive category and solvent vapor emissions which are usually fugitive in nature. The chemical and physical properties of each type will be discussed below.

Considerable effort has been expended to identify the various types of chemical compounds emitted during a varnish cook. The majority of this work was done in the 1950's and is well summarized by R. L. Stenburg in the H.E.W. Technical Report A58-4. Copies of his summaries are included here as Tables 24 and 25.

In general, one or more of the following compounds are emitted, depending upon the ingredients in the cook and the cooking temperature; water vapor, fatty acids, glycerine, acrolein, phenols, aldehydes, ketones, terpene oils, and terpene. These materials are mainly decomposition products of the varnish ingredients.

Solvent vapors account for the majority of the gaseous emission from a paint plant. Some of the relevant properties of the more widely used solvents are given in Table 26. None of these materials are considered exceptionally hazardous. Several, however, have maximum allowable concentration limits as set by OSHA. These are given in Table 27.

Odor thresholds for some of the organic vapors encountered in the paint plants as well as raw materials and trace products which are encountered in resin manufacturing are given in Table 28. They include solvents listed earlier as well as some which might be found in the miscellaneous solvent category.

The carrier gas for all contaminated streams except the resin reactor exhaust will be essentially ambient air. This will be true also for the kettles during charging of reactants. During most of the reaction cycle for the fusion kettle, the carrier gas consists of the sparge gas passed through the reactor. This is produced in the inert gas generator and is approximately 10 to 12% CO_2 and 85 to 90% N_2, on a dry basis. Small quantities of CO may be present along with other trace components normally found in air (argon, etc.) and combustion products. Gas leaving the scrubber-ejectors and the solvent kettle condenser vent will be saturated in water vapor at the operating temperature of the condenser or scrubber.

As discussed earlier, there are a variety of particulate emissions from paint and varnish manufacturing. The major source of these emissions are the pigments and extenders. Representative particle size ranges for the more widely used pigments and extenders are given in Table 29. Maximum allowable concentration limits for these as set by OSHA are given in Table 27.

It can be noted that the thermal settling velocity of a 50 micron diameter particle of specific gravity 2.0 is about 18 cm/sec or 0.6 ft/sec. Particles and agglomerates in this size range or larger should not escape into the surrounding atmosphere during loading. On the other hand, particles smaller than this size that do escape during loading have the potential to be swept out of the building by the ventilation system.

B. Sources of Emissions

1. Major — The major sources of emission are listed on page 100.

TABLE 24

COMPOSITION OF OIL AND VARNISH EMISSIONS

Bodying Oils	Running Natural Gums	Manufacturing Oleo-Resinous Varnish	Manufacturing Alkyd Varnish
Water vapor	Water vapor	Water vapor	Water vapor
Fatty acids	Fatty acids	Fatty acids	Fatty acids
Glycerine	Terpenes	Glycerine	Glycerine
Acrolein	Terpene oils	Acrolein	Phthalic anhydride
Aldehydes	Tar	Phenols	Carbon dioxide
Ketones		Aldehydes	
Carbon dioxide		Ketones	
		Terpene oils	
		Terpenes	
		Carbon dioxide	

TABLE 25

ODOR AND COMPOSITION (BY FUNCTIONAL GROUPS) OF OIL AND VARNISH EMISSIONS

Process and Temperature	Kettle Ingredients	Compounds Identified	Odor
Heat Polymerization of Linseed Oil 575°F	Linseed Oil Admoline (a catalyzed Linseed Oil)	Saturated and/or unsaturated: Aliphatic Fatty acids Aldehydes Aliphatic Esters Paraffins Olefins	
3 Dark Linseed Oil 580°F	Raw Linseed Oil	Saturated and/or unsaturated: Carboxylic Acids Aliphatic Esters Alkyl Aldehydes Paraffins Olefins Unsaturated: Acids Esters Aldehydes	Harsh pungent odor. Characteristic of short chain aldehydes. (Cause eye watering to varying degrees.)
0-Pale Linseed Oil 580°F	Alkali Refined Linseed Oil	Saturated and/or unsaturated: Aliphatic Fatty acids Olefins	
1-Pale Linseed Oil	Alkali Refined Linseed Oil	Saturated and/or unsaturated: Fatty Acids Saturated Aldehydes Olefins	
00-Pale Linseed Oil 580°F	Alkali Refined Linseed Oil	Saturated and/or unsaturated: Aliphatic carboxylic acids Unsaturated Alkane Esters Saturated Alkyl Aldehydes Olefins	
Tall Oil Alkyd 475°F	Tall Oil Glycerine Fumaric Acid	Saturated and/or unsaturated: Carboxylic acids Esters Aldehydes Alcohols Paraffins Olefins Fumaric Acid	Hydrogen Sulfide (Rotten egg odor).

TABLE 25 (continued)

Process and Temperature	Kettle Ingredients	Compounds Identified	Odor
Tall Oil Alkyd 560°F	Tall Oil Glycerine Pentaerythritol		Very Offensive —Hydrogen Sulfide, n-Butyl Mercaptan (Skunk Odor).
Soybean Oil Alkyd 475°F	Soybean Oil Glycerine Fumaric Acid Rosin	Saturated and/or unsaturated: Aliphatic carboxylic acids Aliphatic Alcohols Alkyl Aldehydes Alkane Esters Paraffins Olefins	Mild soapy and slightly lemon-like odor.
Linseed Oil Alkyd 475°F	Alkali Refined linseed oil Glycerine Phthalic Anhydride Litharge	Aromatic Acids Aromatic Esters Aromatic Aldehydes Aliphatic Carboxylic acids Aliphatic Aldehydes Aliphatic Alcohols	Typical linseed oil cooking odors (harsh and stinging).

TABLE 26

SOLVENT CHARACTERISTICS

Solvent	Molecular weight	Vapor pressure, mm Hg 20°C	Vapor pressure, mm Hg 100°C	Boiling point* °C
Mineral spirits	160 (est.)	2 (est.)	30 (est.)	–
Xylene	106	7.1	250	–
Toluene	92	22	580	–
Methanol	32	92	–	64.7
Ethanol	42	43	–	78.4
n-Butanol	74	4.3	400	–
Acetone	58	186	–	56.5
MEK	72	80	–	79.6
Ethyl acetate	88	56	–	77.1

*For solvents that boil below 100°C

TABLE 27

MAXIMUM OSHA ALLOWABLE CONCENTRATION LIMITS

Material	Maximum allowable exposure (8 hour weighted average)
Ethyl Acrylate	25 ppm
n-Butanol	100 ppm
Phthalic Anhydride	12 mg/m^3
Toluene	200 ppm*
Xylene	100 ppm
Carbon black	3.5 mg/m^3
Talc (non-asbestos form)	20 particles/cm^3
Talc (asbestos form — Tremolyte)	5 fibers/cm^3**
Inert dust	
Respirable	5 mg/m^3
Total	15 mg/m^3

*Will change to 100 ppm in near future

**Will change to 2 fibers/cm^3 in 1976

Source: Fed. Reg., Vol. 37, No. 202, 1972. Additional information available from this source.

TABLE 28*

ODOR THRESHOLDS OF SOME ORGANIC VAPORS

Chemical	Odor threshold, ppm
Acetaldehyde	0.21
Acetone	100.0
Acrolein	0.21
Benzene	4.68
Ethanol	10.0
Ethyl acrylate	0.00047
Formaldehyde	1.0
MEK	10.0
Methanol	100.0
Methyl methacrylate	0.21
Methylene chloride	214.0
Phenol	0.0470
p-Xylene	0.47
Styrene (inhibited)	0.10
Styrene (uninhibited)	0.047
Toluene	2.14

*Air Pollution Control Assoc. Journal, Volume 19, Number 2, Feb. 1969, pages 91 to 95

TABLE 29

PARTICLE SIZE RANGE OF VARIOUS PIGMENTS AND EXTENDERS[2,4]

Pigment	Size range, microns
TiO_2	0.1 to 1
Extenders	
Silica	0.1 to 20
$CaCO_3$	0.03 to 8
Talc	0.2 to 10
Clay	0.5 to 10
Iron oxides	0.2 to 15
Carbon blacks	0.01 to 0.3

1. Varnish cooking
2. Resin cooking
3. Thinning

They are all non-fugitive and consist primarily of organic vapors including phthalic anhydride, which may or may not be in the vapor state. They are also normally the major source of potential odor nuisance problems.

2. Minor — Minor sources of emissions included are tabulated below:

Location	Fugitive	Non-Fugitive
1. Handling & Storage	Hydrocarbons	
2. Milling Operation	Hydrocarbons, Pigments	Hydrocarbons, Pigments
3. Blending & Finishing	Hydrocarbons	
4. Filling	Hydrocarbons	

On an individual basis, each of these sources can be considered minor. If they were to be collected and vented at a common point, they would constitute a major source. This is demonstrated in more detail in the following section.

C. Quantities of Emission from Uncontrolled Plants

As indicated in Section I, the manufacturing of paint is a very non-standardized industry. The type and quantity of emission will vary significantly from plant to plant. To provide a better representation of the average situation, the model plant presented earlier will be used as a basis for this discussion where applicable. Varnish and resin manufacturing are not well covered in the model plant and the quantity of emissions from these sources will be discussed separately.

1. Model Plant — The model plant has been designed to reflect modern practices and technology as generally applied, rather than the frontiers of technology as practiced by perhaps a few plants.

Likewise, the emissions calculations will assume commonly applied practice and observations. It will further assume that equipment items, such as condensers, have been properly sized and are properly maintained to insure good operation.

Common practice in this context is determined from questionnaire data, literature references, information from equipment manufacturers, and personal experience. Wherever possible, data for plants and equipment similar in size and function to that for the model plant will be used in preference to overall industry averages. Where a system is sufficiently well defined, a theoretical calculation is used to estimate emissions.

A schematic diagram showing the emission points for this model plant are given in Figures 15 and 16. Some tanks are tied in to common vent points as shown.

a. Solvent Emissions From Tanks — This group comprises emission points 1 through 7. It will be assumed that the outside storage tanks (5, 6, 7) are equipped with conservation vents. Since the inside storage tanks (1 to 4) are not subjected to significant daily temperature cycles, these vents are left uncontrolled. Emissions, then, are confined to losses during filling operations. It will further be assumed that xylene is the solvent used for industrial alkyds. Finally an average ambient temperature of 20°C both inside and outside will be specified.

Table 30 summarizes the operating data for the storage tank emission sources. Table 31 lists the calculated emissions for these sources. For sources 1, 2 and 3 it is assumed that the vapor pressure of the solvent over a resin solution is half that of the pure solvent. Similarly, the waste solvent is assumed to be 50% xylene and the rest primarily mineral spirits. The vapor pressure over this is taken as 50% that of pure xylene with the contribution of the mineral spirits neglected. The emissions were calculated by converting the turnover in gallons to cubic feet and determining the amount of solvent present in that number of cubic feet of gas saturated with solvent vapor at the appropriate vapor pressure. Table 31 also gives the instantaneous emission rate assuming liquid is pumped into the tank at 100 gallons per minute. Total emissions from these sources amount to 184.8 pounds per year. Emission rates run as high as 2.06 pounds per hour at 100 gallons per minute input filling rate.

b. Manufacturing Area — The manufacturing area emissions consist of sources 8 and 9. Upper floor manufacturing area includes the mills, mixers, finishing tanks, etc. The lower floor includes the filling area as well as the ambient air around the resin plant and indoor storage tanks. It does not include the thin tank and resin reactor vents themselves as these will be considered separately. The emissions from the manufacturing areas exit as part of the exhaust from the ventilation system.

The ventilation system for the model plant was designed to produce six air changes per hour. This converts to an exhaust rate of 48,400 cfm for each of points 8 and 9. The Canadian Paint Societies has discussed a model plant in which ventilation requirements were set at 2 cfm per ft^2 of floor area.[10] The present situation compares well at 2.2 cfm per ft^2. In order to determine the emission rate for these sources, it is necessary to estimate the concentration of pollutants in the exhaust gas stream.

An examination of the questionnaires reveals two plants which present data that is usable

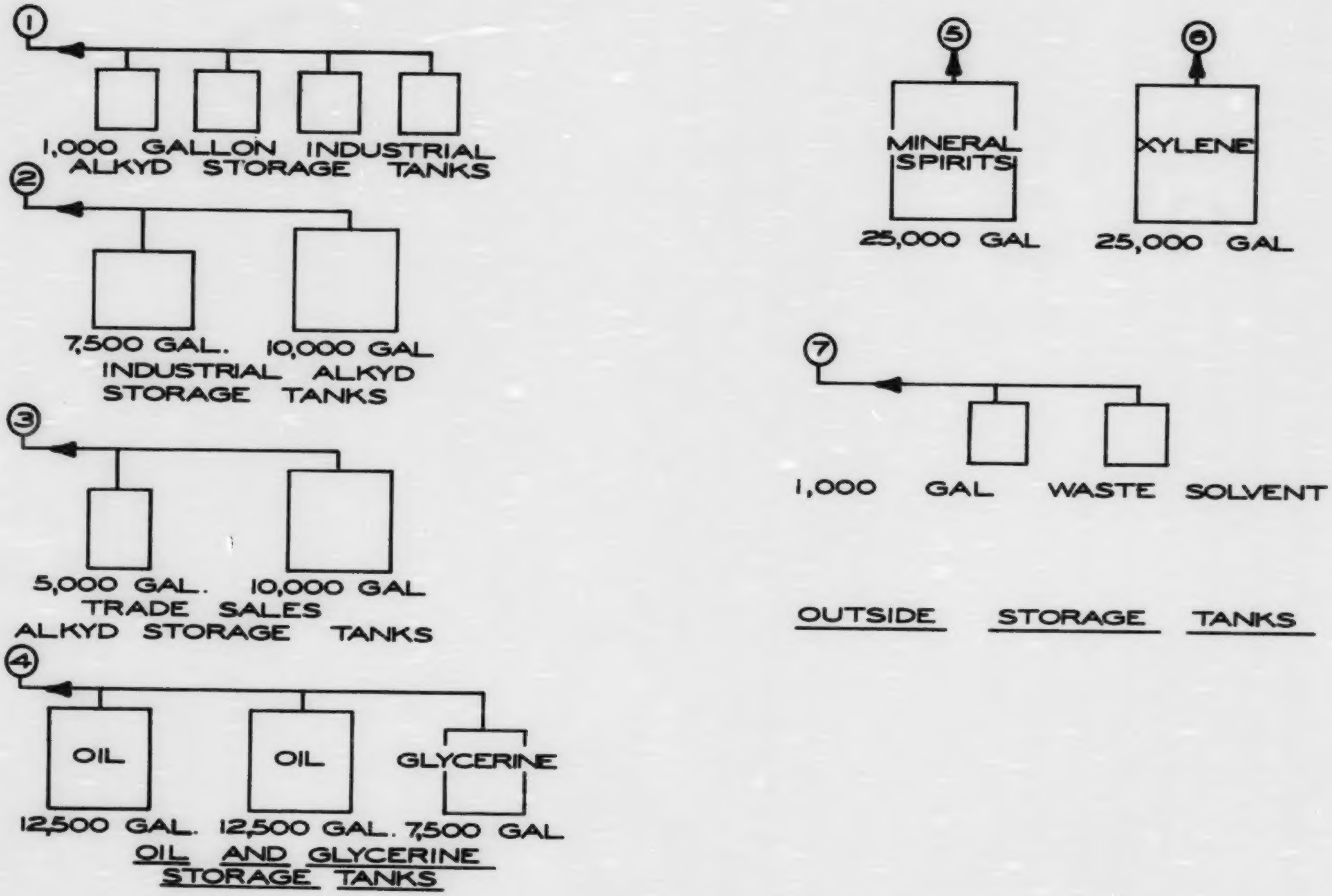

FIGURE 15

EMISSION POINTS FROM RAW
MATERIAL STORAGE TANKS
OF MODEL PLANT

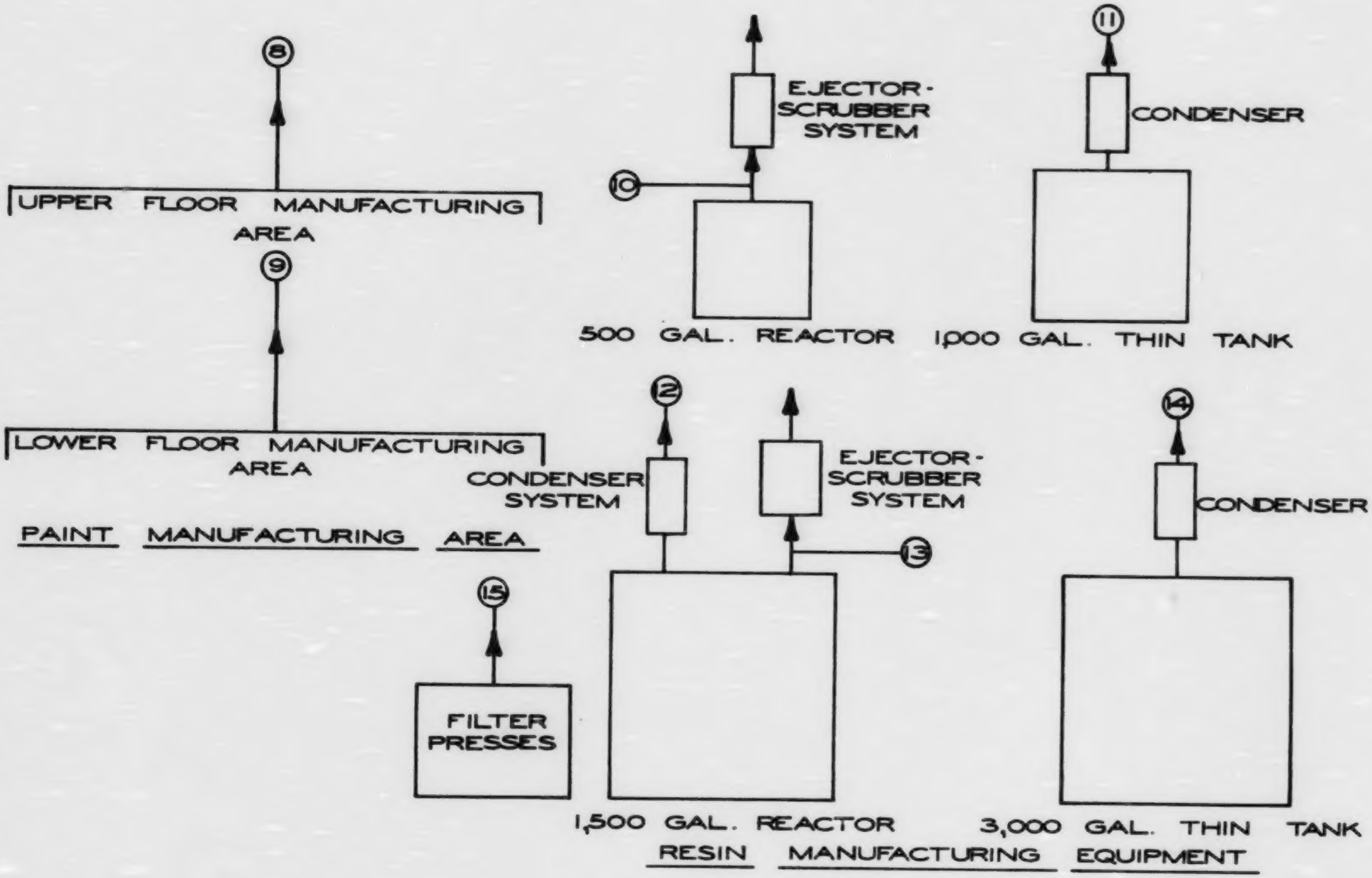

FIGURE 16

EMISSION POINTS FROM PRODUCTION AREAS OF MODEL PLANT

TABLE 30

OPERATING PARAMETERS FOR MODEL PLANT

STORAGE TANK EMISSION SOURCES

Emission point	Tankage	Material stored	Turnover (gal/yr)
1	4,000	Industrial alkyd (50% NVM)	53,000
2	17,500	Industrial alkyd (50% NVM)	232,000
3	15,000	Trade alkyd (50% NVM)	257,000
4	32,500	Oil, glycerine	188,200
5	25,000	Mineral spirits	216,000
6	25,000	Xylene	234,000
7	2,000	Waste solvent (50% xylene)	30,900

TABLE 31

EMISSIONS DURING FILLING FOR MODEL PLANT STORAGE TANKS

Emission point	Principal emission	Amount (lb/yr)	Concentration (ppm)	@ 100 gal/min input to tank	
				Exhaust rate (ACFM)	Emissions (lb/hr)
1	Xylene	9.1	4,700	13.4	1.03
2	Xylene	39.8	4,700	13.4	1.03
3	Mineral spirits	18.7	660	13.4	0.44
4	Oil, glycerine	nil.	nil.	13.4	nil.
5	Mineral spirits	31.5	1,300	13.4	0.87
6	Xylene	80.4	9,350	13.4	2.06
7	Xylene	5.3	4,700	13.4	1.03
Total		184.8			

for estimating exhaust gas contaminant levels. These companies reported the solvent vapor concentrations in the air at various locations in their plants. The first plant (Plant A) produces almost one million gallons per year of which 80% is solvent based.

The second plant (Plant B) is a 2.5 million gallons a year facility with 55% solvent based. The results from this questionnaire are also summarized in Table 32.

Based on this data, an emission level of 15 ppm in the exhaust from the upper floor production area (Source 8) should not be an unreasonable estimate. This allows for averaging and dilution from parts of the area which show low solvent vapor levels. A level of 5 ppm will be used to estimate the levels from the lower floor production area (Source 9). The calculated emissions for those sources are given in Table 33. The total for these two sources is 63,500 pounds per year.

Only one plant reported sufficient data in the questionnaires to provide a basis by which the model plant emissions can be compared to existing plant emissions. This plant produces 2.7 million gallons per year of coatings (all solvent based). The production areas corresponding to points 8 and 9 of the model plant have ventilation rates which together total 35,800 cfm (versus 96,800 cfm for the model plant). This plant reported emissions from these areas of 62,660 pounds per year. The emissions for the model plant, per million gallons of paint produced, in comparison are higher. At least some of this difference can be attributed to the considerably higher ventilation rate in the model plant.

No estimate has been made for particulate emissions from these sources. The absence of ducts and hoods specifically for the purpose of dust collection means that a large part of the pigment dust which escapes into the air will tend to settle out inside the plant. The ventilation system will not provide air velocities sufficiently high to capture any but a portion of the particulate. It would be very difficult to estimate the pigment emission from the plant, as presently designed, by comparing data reported for hooded and locally exhausted systems.

c. Resin Production — Emissions from the 500 gallon fusion reactor are of two types: (1) Those that occur during sparging; and (2) those that occur during loading when the hatch is opened. The ejector-scrubber is in operation at all times during the cook. The emission levels that will be estimated for this reactor are those at point 10, the reactor outlet vent and before the scrubber. At the present time, insufficient information is available to estimate emissions downstream from the scrubber.

It is expected that the small reactor will be used primarily to process small batches of

TABLE 32

CONTAMINANT LEVELS IN VARIOUS PARTS OF MODEL PAINT PLANT

		Concentration, ppm			
Plant	Location	Toluene	Xylene	MEK	MIBK
A	Can filling area	12.0	12.0	24.0	–
A	Center, mixing area	6.0	10.4	23.2	–
A	Center, mixing area	6.0	54.4	12.0	–
A	Tank cleaning area	6.0	58.0	–	–
A	Near large holding tanks	6.0	7.3	54.6	6.0
		Toluene	Xylene	Acetone	
B	Portable tank area	7.6	3.8	29	
B	Filling area	4.5	2.2	13	
B	Mixing area	10	10	–	

TABLE 33

EMISSIONS FROM MODEL PLANT PRODUCTION AREA EXHAUST

	Source 8	Source 9
Exhaust rate, cfm	48,400	48,400
Principal contaminant	Xylene	Xylene
Concentration, ppm	15	5
Emissions, lb/hr	11.9	4.0
Emissions, lb/yr	47,500	16,000

specialty industrial alkyds. For illustrative purposes, a "typical" batch will be assumed to consist of a short oil formulation charge to the reactor at 2,500 pounds of raw materials. A total run time of 8 hours is considered representative with 3 hours allowed for alcoholysis and 5 hours for esterification.

A "typical" log for this process follows:

Time, hr	Temperature, °F	
0	Ambient	Charge reactor with 1,000 pounds of oil, 600 pounds of glycerine. Blanket with inert gas. Agitator and heat on.
1.5	450	Shut off agitator. Add Catalyst.
1.55	430	Agitator on.
1.75	450	Hold at 450°F.
3.00	450	Alcoholysis complete. Agitator off. Cool slightly.
3.10	400	Add 900 pounds of phthalic anhydride. Agitator on. Sparge at 10 cfm.
3.30	450	Hold at 450°F for esterification.
5.10	450	Sparge at 5 cfm.
6.10	450	Sparge at 2.5 cfm.
7.50	450	Esterification complete. Cool.
8.00	400	Agitator, sparge off. Drop to thin tank.

This log is based on similar information contained in technical literature published by the Brighton Corporation[11] and on information contained in Martens' book.[4] It is hypothetical but reflects the general features of resin plant operation.

Figure 17 presents emission levels, exhaust rates for noncondensibles (air and/or inerts), and water evolved as a function of time. Again, these are hypothetical but are intended to represent general trends and orders of magnitude.

The emission curve is adapted from that presented later in Figure 23 of this report. This represents hydrocarbon ppm (as methane) at the reactor vent for a fusion cook. Concentration is reported on a dry basis. Generally speaking, the analytical method used to obtain this curve does not measure phthalic anhydride, though small amounts may have entered the instrument and been recorded. It represents that portion of the emissions which is virtually unaffected by the scrubber and so provides an estimate of emissions from the scrubber exhaust. It was estimated by the engineer who supervised the source test which produced Figure 23 that a typical scrubber will remove, at most, 10% of these contaminants.

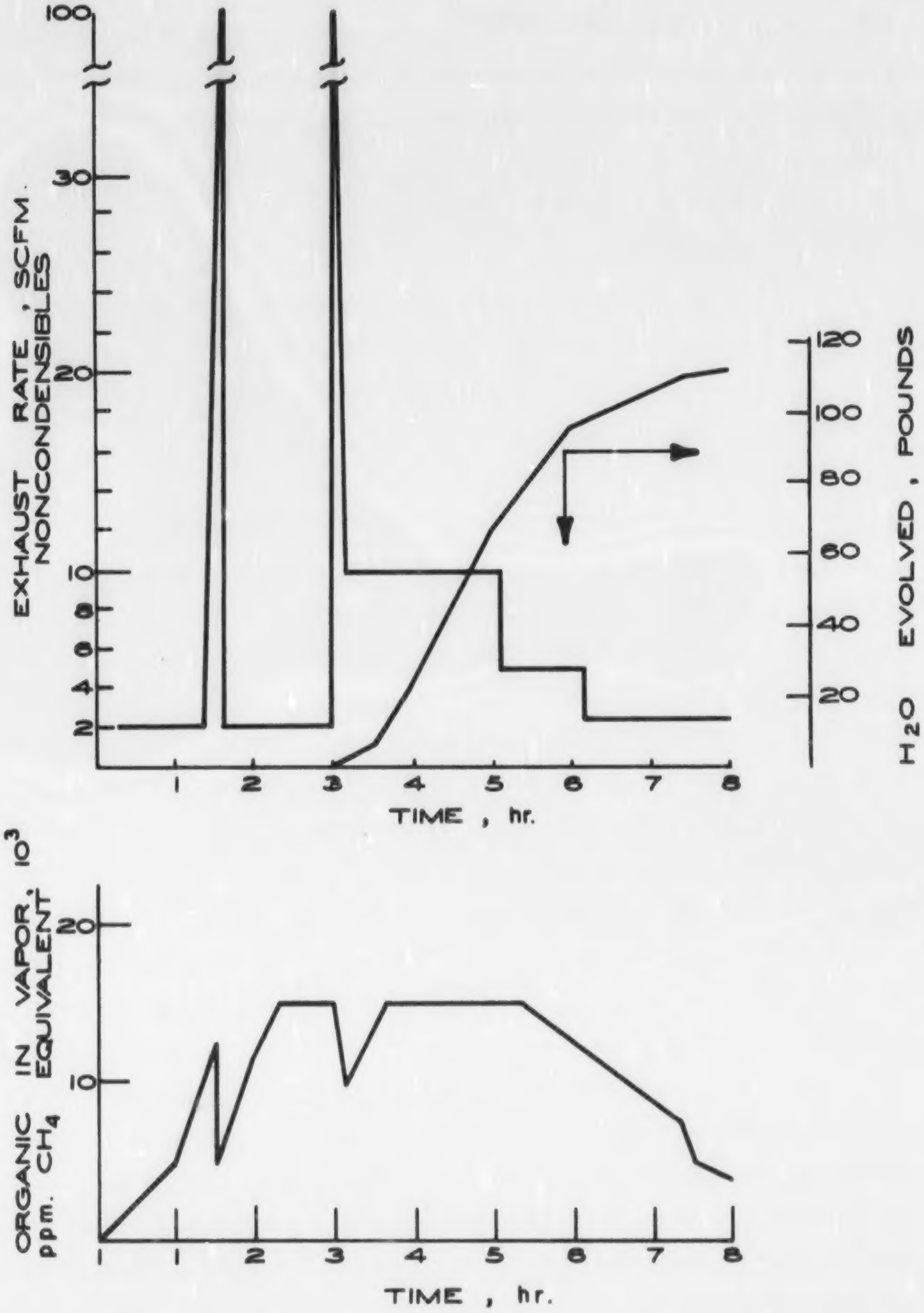

FIGURE 17

EMISSION CHARACTERISTICS – SHORT OIL FUSION COOK

Exhaust rates were based on 2 cfm inert gas blanket during alcoholysis, 0.04 cfm per gallon of charge during the first two hours of esterification, 0.02 during the third hour, and 0.01 for the remainder of the cook. A peak of 100 cfm during charging was assumed based on questionnaire data. The water evolution curve is based on the Brighton[11] information and Martens.[4] It was constructed to reflect the characteristics of a short oil alkyd cook.

The 1,500 gallon reactor is set up for either fusion or solvent cooking. It is expected, however, that solvent cooking will represent the normal mode of operation. A "typical" batch for this reactor will be assumed to be a long oil alkyd formulation charged at 7,500 pounds of raw materials. A total run time of 12 hours, 5 hours for alcoholysis and 7 for esterification will be assumed. A "typical" log for this process is given on the following page.

Figure 18 presents contaminant levels, exhaust rates, and water evolution as a function of time. The contaminant levels and exhaust rates are presented for point 12, the condenser vent. The exhaust rates for noncondensibles is based on questionnaire data. Only a few plants to date have reported exhaust rates from the condenser vent. Values of 2.5 cfm to 7 cfm have been reported for the noncondensibles from kettles of 300 to 3,000 gallons capacity. A value of 0.25 cfm has been chosen to represent the inert gas blanket flow rate for this reactor.*

Maximum emission levels were calculated by assuming that the exhaust from the condenser vent is saturated in xylene vapor at the operating temperature of the condenser. It was assumed that the condenser vent temperature is at 100°F during the peak reaction period and drops slightly towards the end of the cook. At 100°F the vapor pressure of xylene is taken as 18 mm Hg. At 1 atm total pressure, this is equivalent to 24,000 ppm xylene (192,000 ppm as C_1).

The water evolution curve is representative of the shape often observed for long oil alkyds. It reflects the observation that the reaction rate for long oil alkyds is very high initially and then drops off for the remainder of the cook. This can be compared with the curve for the short oil alkyd which shows a more moderate reaction rate which extends for a longer portion of the reaction time.

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*For the two solvent cook source tests shown in Appendix D, noncondensible flow rates average about 0.5 SCFM for one cook and about 0.25 SCFM for the other. These flows were observed *after* the solvent was added and the condenser was turned on. It does not cover the loading and heat-up phase during which the ejector was on.

TYPICAL LOG OF 1,500 GALLON SOLVENT PROCESS REACTOR

Long Oil Alkyd — 60% Oil

Time, hr	Temperature, °F	
0	Ambient	Charge reactor with 4,500 pounds oil. Blanket with inert gas. Agitator and heat on.
2.0	500	Agitator off. Add 1,000 pounds glycerine. Add catalyst.
2.10	450	Agitator on. Inert gas blanket.
2.60	500	Hold at 500°F.
4.50	500	Alcoholysis complete. Cool to 400°F.
5.00	400	Start condenser. Add 350 pounds xylene, 2,000 pounds PA. Agitator on. Inert gas blanket.
5.75	450	Hold at 450°F for esterification.
11.50	450	Esterification complete. Cool.
12.00	400	Agitator off. Drop to thin tank. Condenser off.

As before, this is an adaption of information published by Brighton Corporation and Martens. It reflects the general features for this type of cook.

The reverse peaks in the curves of Figure 18 occur during loading. When the hatch is opened, the scrubber-ejector is turned on. This draws all the exhaust to the scrubber vent and prevents gas from escaping through the condenser. The flow rate to the scrubbers (Point 13) will be expected to be in the 100 to 150 cfm range during loading. It is not possible, with available information, to estimate the emission rates during this time. The rate will probably be rather high for a short period of time and consist primarily of solvent vapors and phthalic anhydride.

The emissions, by weight, for each of the reactors can be determined from the information given in Figures 17 and 18. For a given time period, the exhaust rate and the average hydrocarbon concentration for that time period provides the information necessary to calculate the emissions. This has been done for each reactor and the results summarized in Table 34. It should be noted that the emissions during loading operations are not included since insufficient information is available. It can be expected that the emission rate will be quite high for short periods of time during charging.

Several comments can be made at this time. The emissions from the solvent reactor are proportional to the assumed inert gas flow and strongly dependent on the assumed condenser vent temperature. Source test personnel from air pollution equipment manufacturers report that it is not uncommon for condensers to be in very poor operating condition due to fouling or other

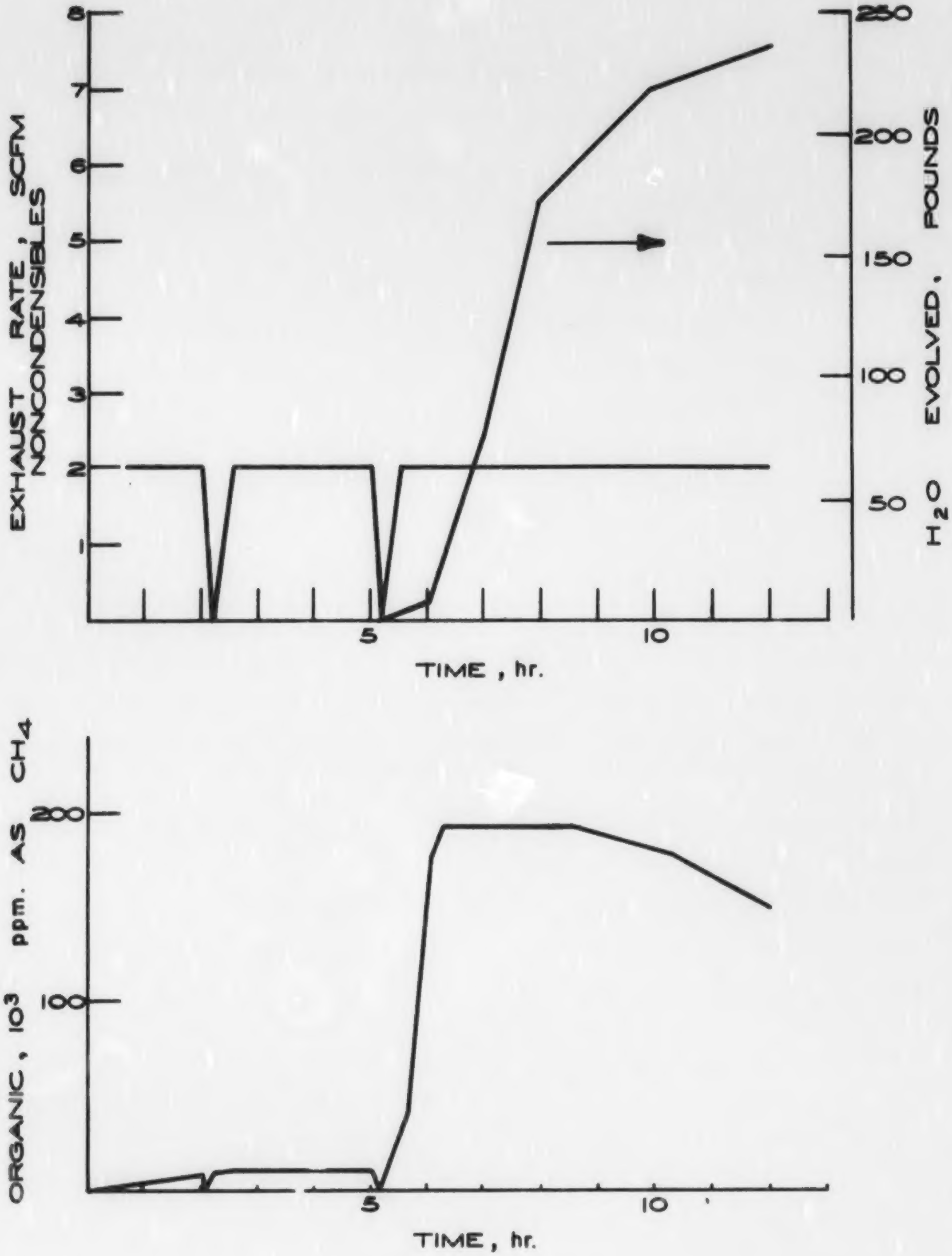

FIGURE 18

EMISSION CHARACTERISTICS – LONG OIL SOLVENT COOK

TABLE 34

SUMMARY OF EMISSIONS FROM MODEL PLANT

500 GALLON FUSION REACTOR AND 1,500 GALLON SOLVENT REACTOR*

	Fusion cook	Solvent cook**
Time of cook, hr	8	12
Total emissions as methane, pounds	1.15	0.7
Max. emission rate, lb/hr	0.41	0.12
Emission per 1,000 pounds charged, pounds	0.46	0.094
Max. emission rate per 1,000 pounds charged, lb/hr	0.16	0.016
Emission per year based on 250 batches/year, pounds	288	175

*The emissions listed here for both fusion and solvent processes are for the "noncondensible" organics. It does *not* include phthalic anhydride, very heavy organics, etc. that are emitted during the baking phases of operation. No reliable data has been located for estimating these latter quantities.

**An average inert gas flow of 0.25 SCFM was used in estimating the solvent process emissions. Many plants operate with essentially no inert gas flow while others may maintain several SCFM. In the former case, emissions will be limited largely to a "breathing flow" situation and will be very small. For the latter case emissions will be much higher than suggested in this table since emissions are roughly proportional to inert gas flow rate.

causes. If the condenser vent in the present instance were operating at 120°F instead of 100°F, the emissions from this source will double.

The inert gas flow through solvent process reactors is also the subject of considerable variation. Among other things, it varies as a function of reactor size and formulation. In some cases, no inert gas flow is used while in others flows as high as 7 cfm have been reported in the questionnaires and 16 cfm in data supplied by one company. Emissions, then, can range from essentially none to several times that calculated for this case.

Finally, the emissions from these kettles were determined for specific cooking formulas using specific process cycles and parameters. Consequently, one should not attempt to draw generalized conclusions concerning the relative merits of solvent versus fusion cooking from the results presented here. They are intended to be specific to the model plant under consideration and are representative of the industry in general only to the extent that the model plant is representative. It may be noted that the results fall within the range reported by one manufacturer as listed in Table 35[12].

d. Thin Tanks and Filter Presses — Emission source points 11, 14 and 15 (Figure 16) will be covered in this category. It will be assumed that each resin is to be thinned to 50% NVM. The thin tanks are equipped with condensers. It will be assumed that the condenser outlet vent operates at 100°F and that the gas is saturated in xylene at that temperature. The gas vented from the thin tank consists of a noncondensible fraction which results from that displaced when the tank is filled. The fusion reactor batch is about 250 gallons while that for the solvent reactor is about 750 gallons. The vapor pressure of xylene at 100°F is about 18 mm Hg. A fairly straightforward calculation gives emissions as xylene of 0.22 pounds per batch for point 11 and 0.65 pounds per batch for point 14. Based on 250 batches per year, yearly emissions will be 55 pounds/year for point 11 and 163 pounds/year for point 14.

The filter presses, taken collectively as source 15, represent a significant source of vapor emissions. It is not possible with presently available information to estimate the quantities involved, however. Vaporized solvent escapes directly into the room air and leaves as part of the room ventilation. Its contribution to emissions is included in the emissions estimated for the lower floor manufacturing area since, as the model plant is conceived, the 48,400 cfm exhaust system for the lower floor area includes the room in which the filter presses and thin tanks are located.

TABLE 35

EMISSION DATA SUMMARY

Resin Type	Reactor Size (gal)	Emission: Range (lb/hr)	Emission: Average (lb/hr)	Major Component	Average Reaction Temp. (^{o}F)	
Alkyds	4,000	0.07 to 1.45	0.7	Xylene	410 to 460	Solvent Cook, based upon 4 resins.
	1,000	0.17 to 0.75	0.3	Xylene		Solvent/fusion cook, based upon 7 resins.
	1,000	0.44 to 1.74	1.0	Xylene		Solvent cook, based upon 4 resins.
						Emissions exceeded 8 pounds/hour during second stage charging.
Polyester	4,000	1.32 to 27.3	12.9	Propylene Glycol	400 to 410	Fusion cook, based upon 4 resins.
						Emissions exceeded 8 pounds/hour during charging, exotherm, and sparging.
	1,000	0.35 to 2.23	1.18	Propylene Glycol		Fusion cook, based upon 8 resins.
Acrylics, Melamines	4,000	0.06 to 0.21	0.10	Butanol	220 to 250	Solvent cook, based upon 11 resins.
	1,000	0.15 to 0.16	0.15	Butanol		Solvent cook, based upon 2 resins.

TABLE 36

EMISSION SUMMARY FOR GASEOUS CONTAMINANTS — MODEL PLANT

Emission point*			
Number	Description	Principle emission	Annual emissions (lb/yr)
1	Indus. alkyd storage	Xylene	9.1
2	Indus. alkyd storage	Xylene	39.8
3	Trade alkyd storage	Mineral spirits	18.7
4	Oil, glycerine storage	Oil, glycerine	nil
5	Min. spirits storage	Mineral spirits	31.5
6	Xylene storage	Xylene	80.4
7	Waste solvent storage	Xylene	5.3
8	Upper floor vent	Xylene	47,500
9	Lower floor vent	Xylene	16,000
10	Fusion reactor	Mixed organics	288
11	Thin tank	Xylene	55
12	Solvent reactor	Xylene	175
13	Solvent reactor	Xylene, PA	undetermined
14	Thin tank	Xylene	163

*Refer to Figures 15 and 16 for locations of these points in model plant.

e. Summary — Table 36 presents yearly emissions by point sources as defined in Figures 15 and 16. The total for these sources is 65,590 pounds per year.

It should be realized, of course, that certain assumptions were made in calculating each of the emissions. In order to understand the numbers, one must have a thorough understanding of the nature of these assumptions and the methods of calculation. The effects of small changes can sometimes be rather dramatic. For instance, a few ppm difference in the contaminant level assumed for the manufacturing area exhaust systems (Point 8 and 9) can make a considerable difference in the emissions from these sources. Likewise, as discussed earlier, emissions from the resin plant are sensitive to the exact operating conditions.

The total gaseous emissions consist almost solely of solvents. They represent 1.7% of total solvents consumed.

2. Varnish and Resins Production — No varnishes and a relatively small portion of resins used in the model plant are produced in the model. Production of these materials is discussed in more detail below.

Varnishes and oils are cooked or bodied at temperatures from 200 to 650°F. At about 350°F decomposition begins and continues throughout the cooking cycle which normally runs between 8 and 12 hours. The quantity, composition and rate of emissions depend upon the ingredients in the cook as well as the maximum temperature, the length, the method of introducing additive, the degree of stirring and the use of inert gas blowing. In general the emissions will average between one to three percent of the charge in oil bodying and three to six percent in varnish cooking[17].

The exact amount of non-fugitive emissions for open kettle varnish cooking is not of great significance for two reasons. First, the amount of varnish cooked in this fashion is quite small and is declining. Secondly, modern varnish reactors are equipped with reflux and water cooled condensers which provide better control of the extent of emission. Of more importance are the characteristics of the emissions related to ease of removal by the applicable pollution control devices.

Modern resin reactors and varnish cookers account for the majority of paint vehicle production in the paint and varnish industry. As described earlier, these products are cooked in larger more carefully controlled reactors equipped with product recovery devices which also help reduce atmospheric emission. As with the old varnish kettles, the amount of emissions vary with the type of cook, the cooking time, the maximum temperature, the initial ingredients as well as the type and method of introducing additives.

The basic methods of cooking used are solvent cooking and fusion cooking. The original and still widely used method is fusion cooking.[2] In this method the ingredients are heated together without solvents at temperatures of 435 to 485°F. This type of process has the maximum emission level caused primarily by the blowing of inert gas through the reactor to remove the water of reaction. Refluxing is required when volatile monomers such as styrene are employed. Fusion cooking is the fastest method for the production of polyester resins other than the alkyd resins.

Solvent cooking is the more modern and now popular cooking method. In this process a small portion of aromatic solvent, usually 4 to 10% is added with the charge or after alcoholysis in the two-stage procedure. The solvent is condensed and refluxed to a decanter for water separation and then returned to the reactor. The main advantages of solvent cooking are faster removal of reaction water, shorter cooking time for alkyd resins, better control of temperature, as well as reduction of hydrocarbon emissions and phthalic sublimation. The condensers must be run warm enough to prevent fouling by condensed phthalic anhydride or phthalic acid so some hydrocarbon emissions are unavoidable.

A considerable amount of emission source testing has recently been completed by suppliers of air pollution control devices on closed kettles or reactors. These efforts have been directed primarily towards quantifying the emissions rather than qualifying them. Recent nationwide hydrocarbon emission surveys of a large resin manufacturer indicated that better than 85% of the reactor emissions were materials originally charged to the reactor.[18] A similar conclusion without exact percentages was indicated by W. G. Skelly in his report covering the analysis of potential sources of odor and pollutants from the Bensenville, Illinois plant of Stresen-Reuter International.[19]

From an air pollution control engineering design standpoint, the conclusions above are the major significant result of the above tests. The rest is mainly of academic interest. Assuming thermal or catalytic incineration as the best control device, the type of information required is exhaust rate, temperature, maximum hydrocarbon concentration or Btu loading, and particulate aerosol or condensible hydrocarbon concentration. The hydrocarbon concentration is required to calculate the heat released or system temperature rise from incineration of the fumes. This is required to assure proper sizing of the system, burner, heat exchanger, and residence chamber. Particularly, aerosol and condensible hydrocarbon concentrations are required to prevent condensation in the connecting ductwork and heat exchanger or unit inlet, which will eventually lead to plugging, loss of adequate ventilation and/or system fires or explosions.

For solvent cooking the quantity of emission does not vary significantly with the size of the reactor but is rather more a function of the volatility of the solvent being used and the size and/or efficiency of the condenser. Since there is less sparge gas used in solvent cooking, exhaust volumes are small (less than 1 SCFM) and consist primarily of noncondensibles. Emissions except when charging will run from 0.1 to 0.5 pounds per hour and will be less cyclic in nature than for fusion cooks.

Emissions during fusion cooking run much higher and vary with size of the reactor. The total exhaust volume is dependent primarily on the sparge rate of inert gas. Dean H. Parker[5] indicated typical sparge rates of 0.04 cfm/gal of charge during the first hour, 0.02 cfm/gal during the second, and 0.01 cfm/gal during the remainder of the cook. The exhaust rate will average from 2 cfm/100 gallons of capacity on small reactors to 1 cfm/100 gallons of capacity on large reactors. A summary of source test results from a variety of resin reactors is presented in Table37.[20]

Since fusion cooking is a cyclic batch process, the concentration of emission will vary from the start to finish of the cook. Hydrocarbon concentration will vary from 15,000 to 80,000 ppm as methane equivalent, depending on the time of the cycle and the type of cook. There are at least 100 different emission curves that could be encountered if one tried to cover all of the different cooking formulas. Particulate phthalic anhydride (PA) is also emitted from the kettle and concentration levels vary depending on cycle time, type of cook, method of charging and type of PA used. Charging of liquid PA rather than dry solid PA significantly reduces the emission rate. Maintaining the linear velocity of the sparge gas below 150 ft/min will also reduce the carryover of PA. Entrained and sublimed PA will run between 1 to 3 pounds per hour over a period of 50 to 70 minutes during and following the charging period. When isophthalic acid is used these types of emissions are reduced.

Details of emission levels from varnish and resin kettles are presented in Table 37 and Figures 19 thru 24 and discussed below.

The 500 gallon reactor shown in Figures 19 and 20 had no reflux condenser and no separate thinning tank. Thinning was done in the reactor. The combination of these two deviations from normal practice accounted for the high emission rates. Corrective action has been taken.

The 1,000 gallon reactor shown in Figures 21 and 22 is equipped with a reflux condenser and separate thinning tank. This kettle is used for both solvent and fusion cooks. As indicated on Figure 22 the kettle is run blocked-in during most of the solvent cook, and there are no significant emissions until the vent is opened after the batch has been dropped to the thin tank.

The 1,500 gallon kettle shown in Figure 23 has no reflux condenser. It is used for fusion

TABLE 37

SOURCE TEST SUMMARY FOR PAINT PLANT

Kettle Type – Capacity	Type of cook	Maximum volume SCFM	Maximum hydrocarbon ppm CH_4	Maximum emission rate lb/hr*	Remarks
Closed — 1,500 gals (See Figure 23)	Fusion	108	15,000	4.10	No reflux condenser
Closed — 2,500 gals (See Figure 24)	Fusion	105	43,000	11.42	Kettle also used for solvent cooking
Closed — 1,000 gals (Not plotted)	Reflux	336	50,000	42.50	Emission levels during dropping
(See Figure 21)	Fusion	100	30,000	7.59	
(See Figure 22)	Reflux	320	3,000	2.29	Vented only at beginning of run and during dropping to thin tank
Closed — 500 gals (See Figure 19)	Fusion	470	50,000	59.45	Cooks thinned in kettle
(See Figure 20)	Fusion	635	25,000	40.16	Kettle has no reflux condenser
Open — 60 gals	Melt	6,100	180	2.79	Cook time one hour
Open — 60 gals	Lime	7,500	1,800	34.16	Cook time one hour
Open — 60 gals	Wood oil	6,800	180	3.10	Cook time one hour

*These are maximum emission rates and not averages of emission during a cook.

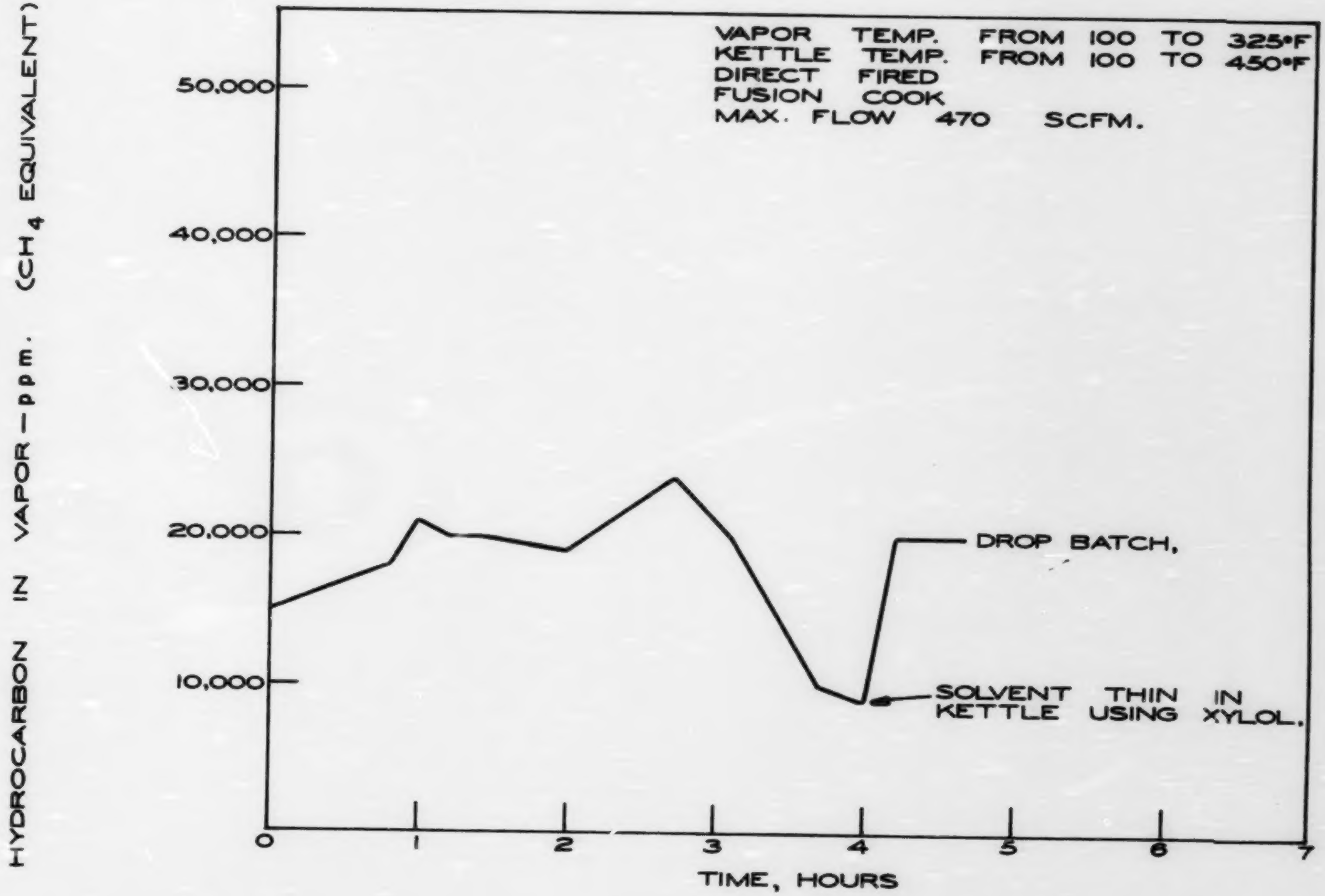

FIGURE 19

HYDROCARBON EMISSION FOR 500 GALLON, CLOSED KETTLE

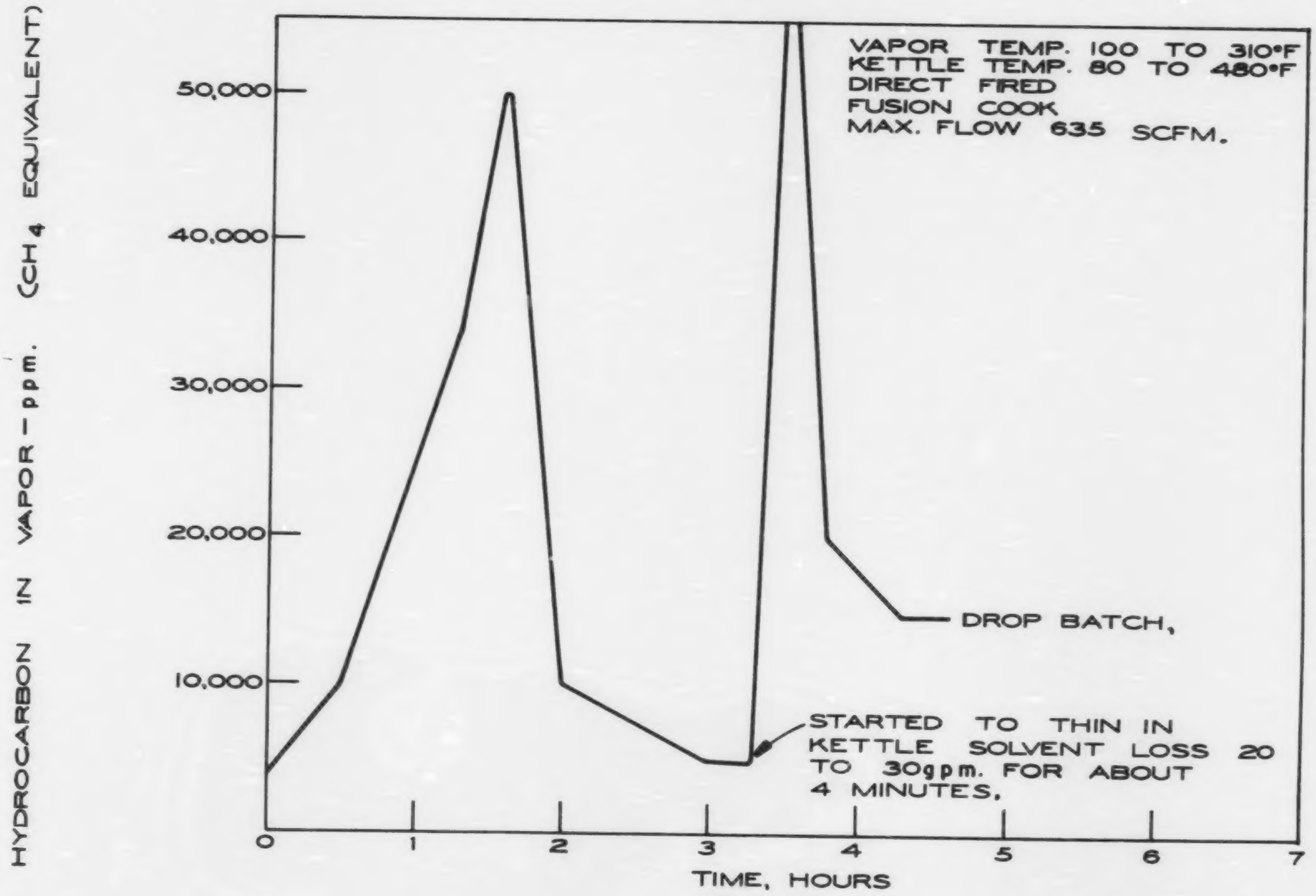

FIGURE 20

HYDROCARBON EMISSION FOR 500 GALLON, CLOSED KETTLE

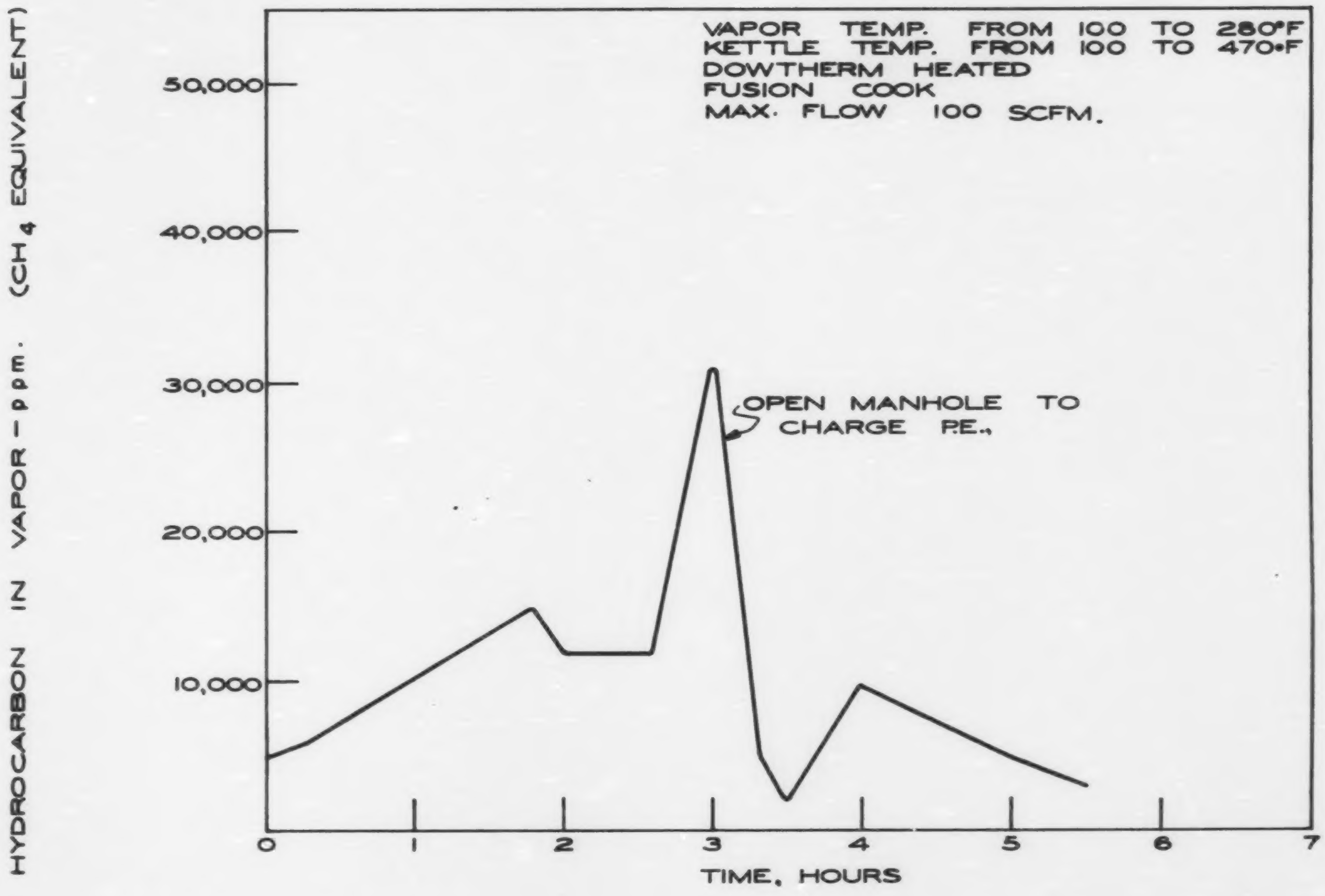

FIGURE 21

HYROCARBON EMISSION FOR 1,000 GALLON, CLOSED KETTLE

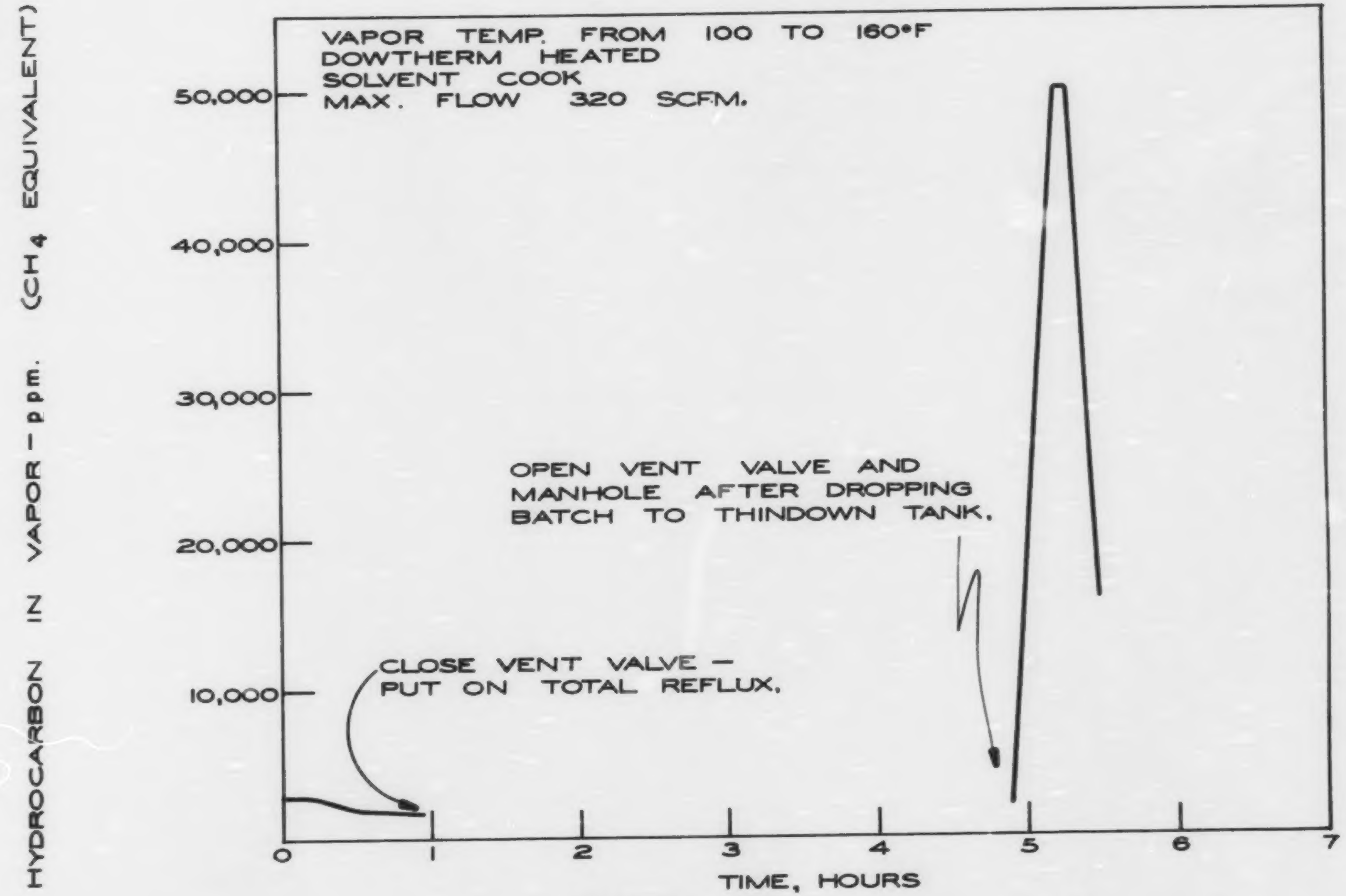

FIGURE 22

HYDROCARBON EMISSION FOR 1,000 GALLON CLOSED KETTLE

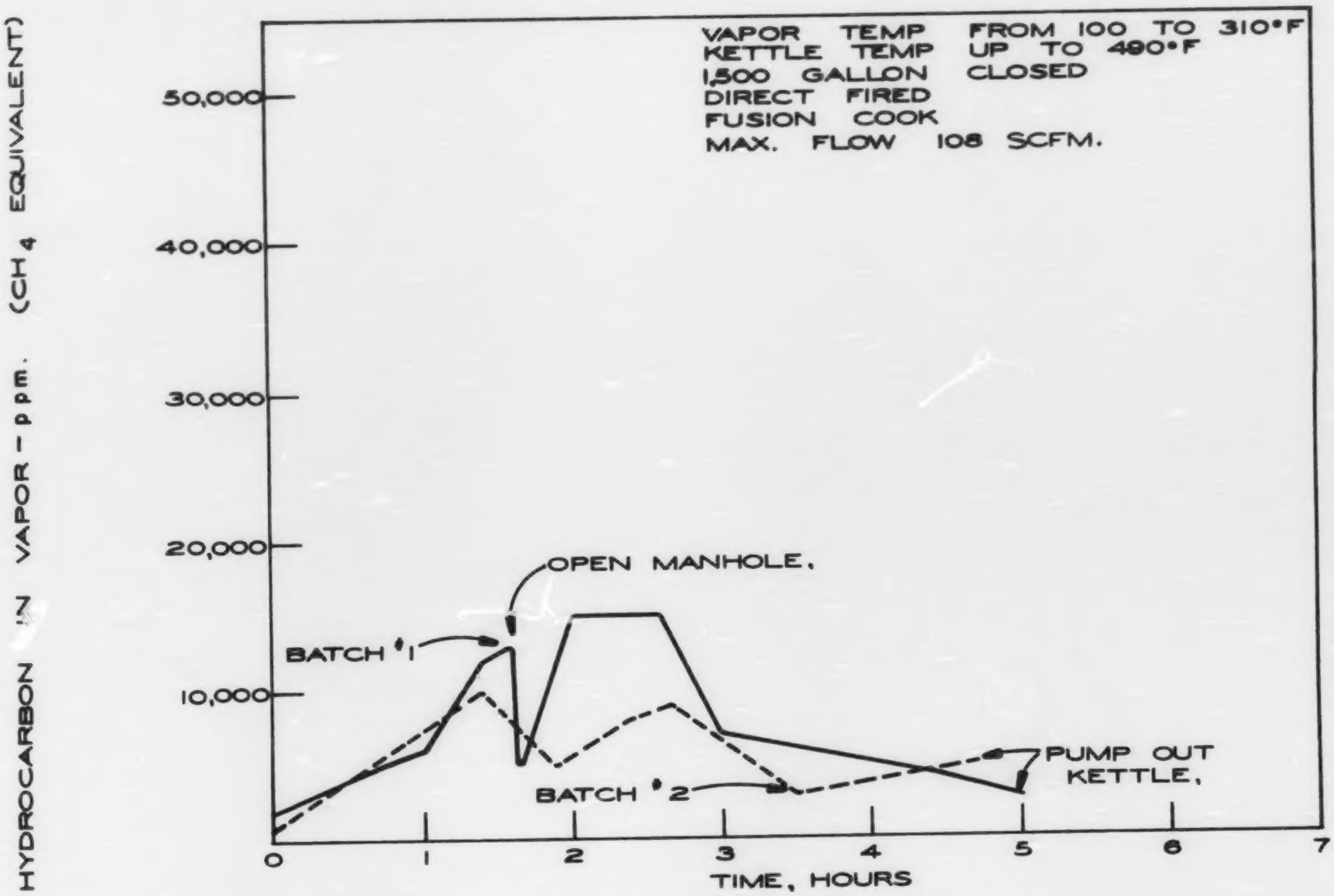

FIGURE 23

HYDROCARBON EMISSION - 2 BATCHES MONITORED

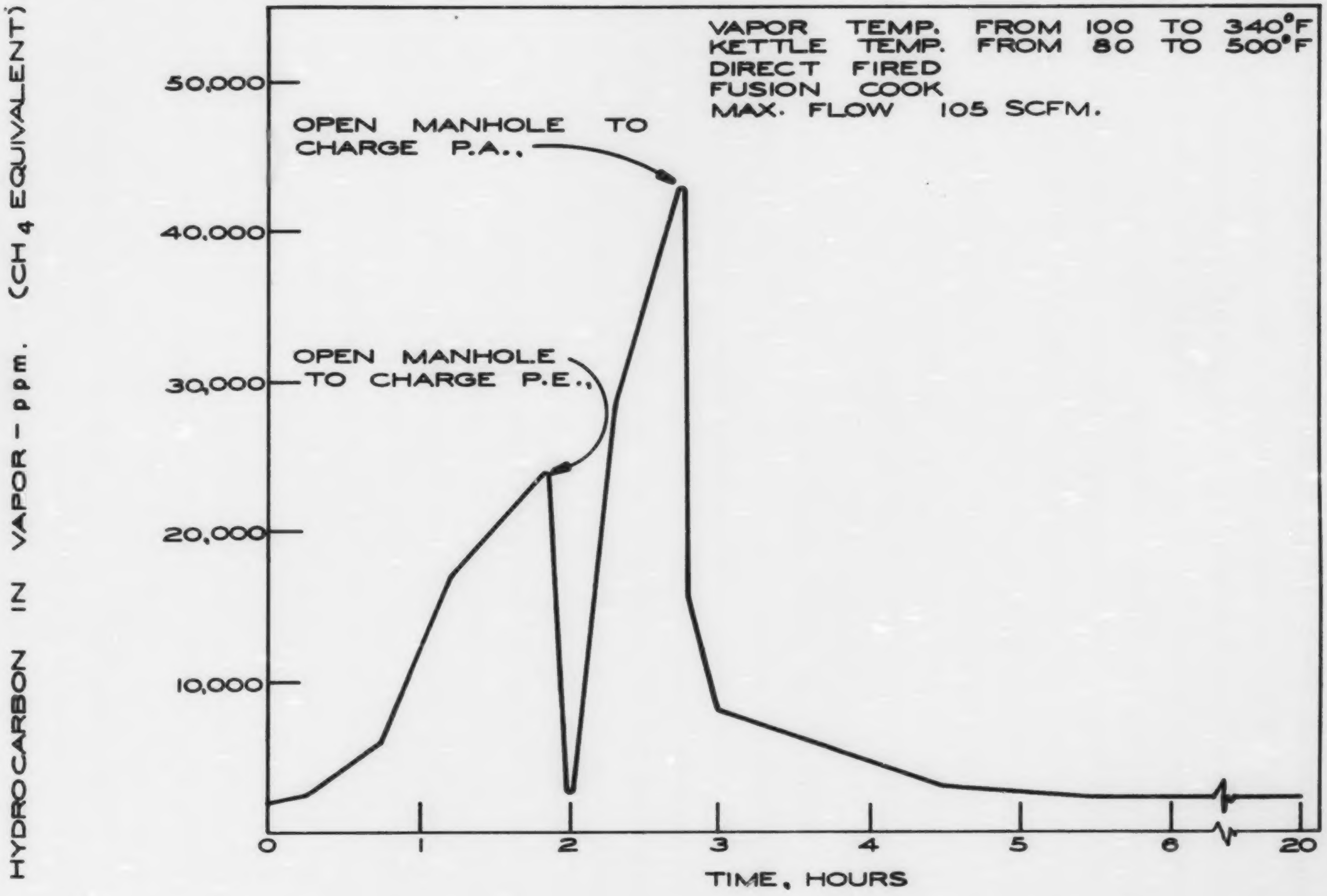

FIGURE 24

HYDROCARBON EMISSION FOR 2,500 GALLON, CLOSED KETTLE cooks only. Thinning is done in a separate tank. Hydrocarbon emissions from the fusion cook shown on Figure 23 are lower than previously plotted fusion cooks and more in line with what might be considered normal emissions. It is felt that this kettle runs with lower emissions since solvent is never added to the kettle or conversely that the other fusion cooks have higher than normal emissions since solvent cooks are interdispersed with the fusion cooks.

The 2,500 gallon kettle shown in Figure 24 has a reflux condenser and thin down tank. It is used for both solvent and fusion cooking and as indicated above has higher emission than those shown on the kettle used for fusion cooking only.

Measurements of emission from three 60 gallon open varnish kettles were also completed. The data is reported at the bottom of Table 37. In general, concentrations were below 220 ppm except during the addition of lime to the 60 gallon lime cook. At this time there was a peak emission of 1,800 ppm for about a one minute period.

It is also of interest that no increase in emission was measured during cooking of the wood oil cook. Cooling was accomplished by the addition of one gpm of water for a three minute period.

The hydrocarbon concentration reported was calculated on a dry basis. A modified M—S—A Total Combustibles Analyzer was used in measuring the hydrocarbon concentration. The instrument was preceeded by a filter to prevent the cells from becoming fouled. This would tend to make the readings presented low by the amount of PA and other heavy organics that might come out in the filter. In clean applications and for measurement of low hydrocarbon concentrations, such as an incinerator outlet, a portable Delphi Model C Flame Ionization Detector was used. Vent flow rates were measured with a precalibrated orifice and magnahelix gauge.

Emission measurements from other closed kettles are graphically presented in Figures 25, 26, 27 and 28. Figure 25 shows the emission from an epoxy cook. The graph is fairly self-explanatory. Note that the kettle is closed-in and operated at 30 psig pressure for four hours.

Figure 26 shows emission rates from a 2,000 gallon resin reactor processing an alkyd cook by the fusion method. Vent flow during cooking ran at a fairly steady rate of about 12 SCFM. As indicated on the graph there was a decanter foam-over at hour seven when hot PA and solvent were added to the batch. Although this is not normal operation, it is not an uncommon occurrence in the industry.

Figure 27 shows emissions from a 1,500 gallon polyester fusion cook. The graph and accompanying data are self-explanatory and show no unusual features.

Figure 28 shows emissions from two 1,000 gallon closed kettles. One kettle was processing

Time	Hrs	Hydrocarbon (% LEL)	Liquid Temperature (°F)	IG Flow (Meter)	Remarks
8:00 AM	0	—	100	0.2	Start heat up
8:45 AM	3/4	225	450	0.2	Exotherm
9:00 AM	1	270	450	0.2	
9:30 AM	1-1/2	325	440	0.2	
10:00 AM	2	340	450	0.2	
10:30 AM	2-1/2	300	440	0.5	
11:00 AM	3	—	—	0.1	Close vent — add solvent
12:30 PM	4-1/2	—	305	0.1	Pressure up to 24 psig
2:45 PM	6-3/4	275	260	0.1	Vent remained closed until about 2:45 PM

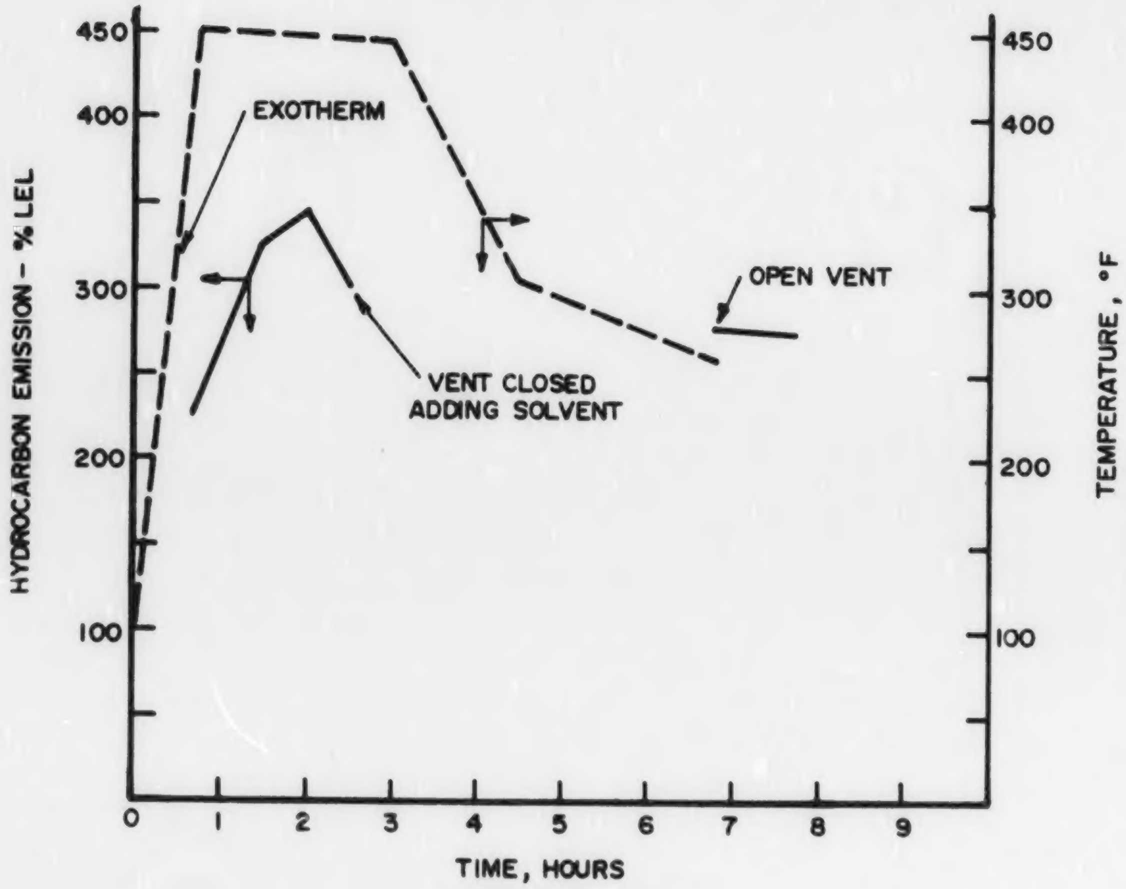

FIGURE 25

EMISSIONS FROM 100 GALLON EPOXY
REACTOR SOLVENT PRESSURE COOK—30 PSIG

Time	Hydrocarbon (% LEL)	IG* Flow (SCFM)	** Emissions (lb/hr)	Remarks
10:20 AM	25	—	--	Prior to sparging
10:30 AM	350	10	4.4	Start sparge
10:45 AM	350	20	8.8	Increase sparge rate
11:00 AM	300	30	11.3	Increase sparge rate
11:30 AM	220	30	8.3	
11:45 AM	150	10	1.9	Make DPG correction addition
12:00 noon	230	30	8.6	Sparge back to normal
1:00 PM	200	30	7.5	
1:30 PM	190	60	14.3	Increase sparge rate
2:00 PM	180	60	13.5	
2:30 PM	180	60	13.5	
3:00 PM	180	80	18.0	Increase sparge rate
3:20 PM	180	80	18.0	

*Flow rate based on rotometer reading.

**Emissions calculated as pounds/hour as methane (based on LEL measurements).

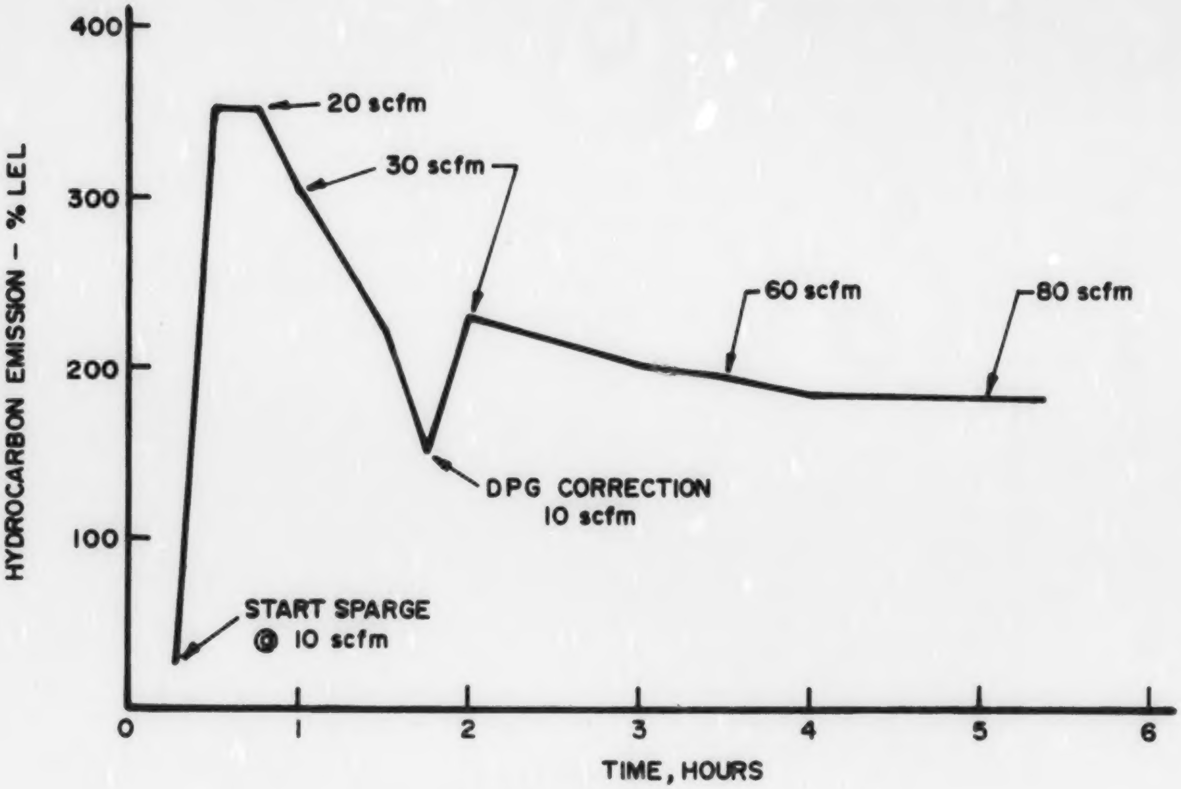

FIGURE 26

EMISSION FROM 2000 GALLON REACTOR

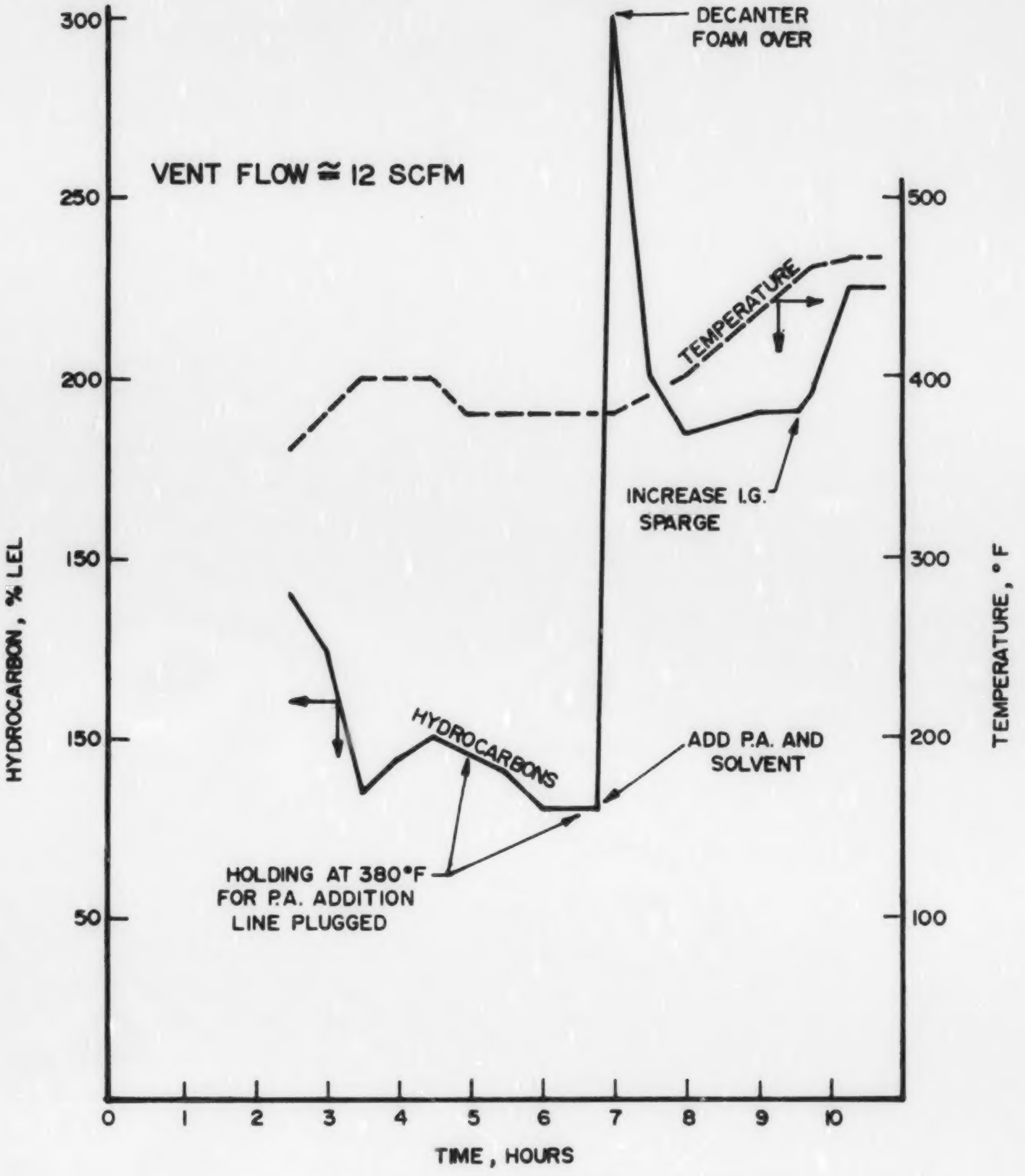

FIGURE 27

EMISSION FROM 1500 GALLON POLYESTER REACTOR FUSION COOK

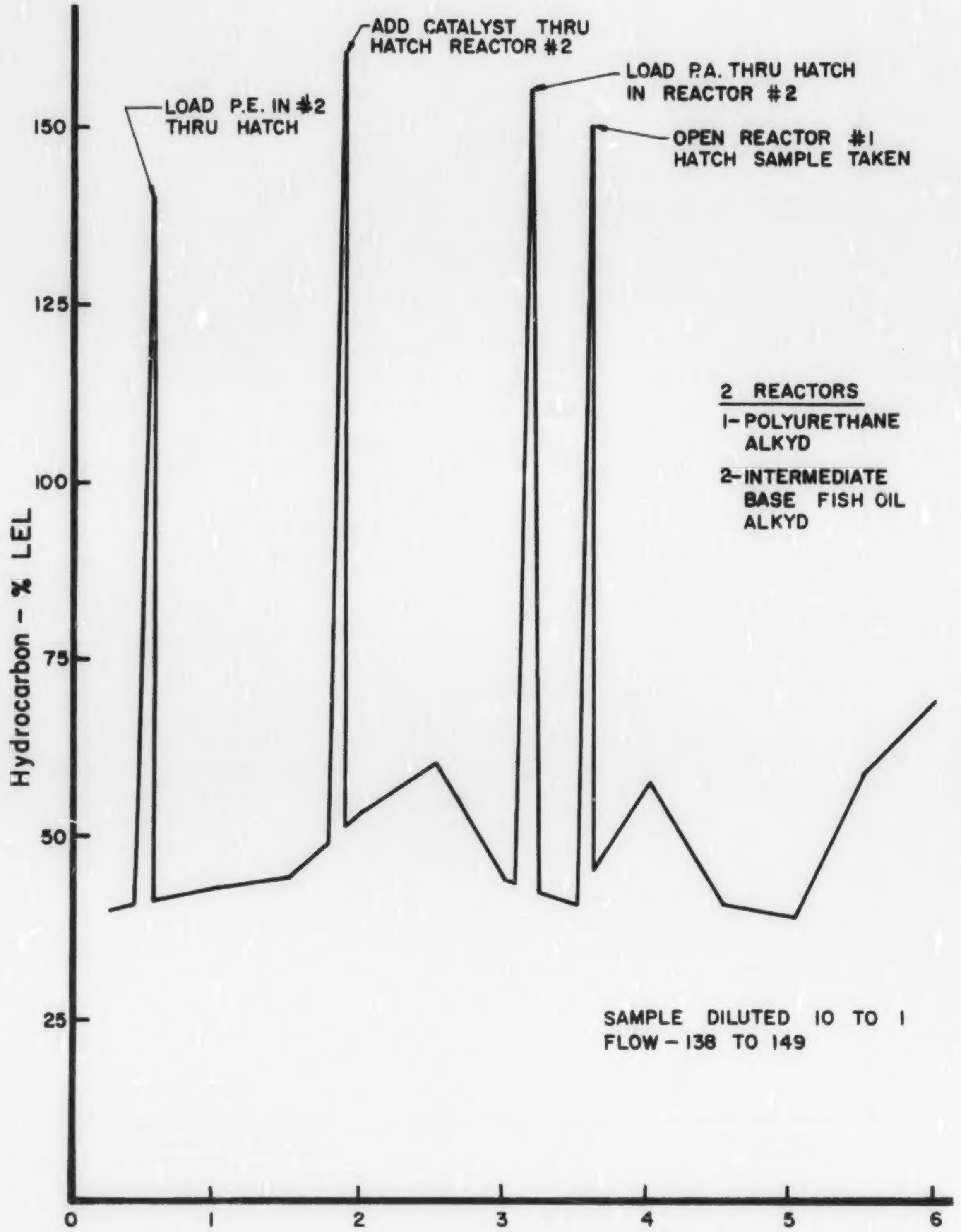

FIGURE 28

EMISSION FROM TWO-1000 GALLON REACTORS

a polyurethane alkyd and the other kettle was processing an intermediate base fish oil alkyd. Measurements were made on the inlet of a 500 SCFM thermal incinerator. The gases from the two kettles were combined and had passed through one water scrubber and one water curtain prior to measurement. It was also diluted about 10 to 1 with air prior to measurement. Flow at the point of measurement was about 150 SCFM as measured by a pitot traverse. The exhaust was further diluted prior to entry into the incinerator. Maximum hydrocarbon emissions ran around 31 lb/hr. As indicated on the graph, there were a number of peak emissions throughout the period of measurement. All were in excess of safe operating limits for the thermal afterburner.

In order to meet requirements of 1/4 LEL (13 Btu/SCF) and thermal incinerator inlet loading requirements of 9 to 12 Btu/SCF emissions are diluted with air prior to being exhausted or sent to a pollution control device. In most cases the streams involved are passed through some type of crude water scrubber to remove heavy oils, resins and condensible phthalic anhydride. The scrubber is normally retained as a pretreatment and safety device if an incinerator has been added for final pollution control. Hydrocarbon concentration after air dilution will run from 1,000 to 4,000 ppm after an adequate water scrubber. Exhaust rates will average around 1,000 SCFM for a 2,500 gallon reactor capacity. This rate will vary significantly, however, if other vent streams from thinning tanks, filter press and the like are included with the exhaust system.

D. Process Operations Influencing Emissions

1. Equipment and/or Process Characteristics

a. Handling and Storage — Materials handling activities are of two types: liquids and dry solids. Bulk liquids are transferred wherever possible through pumps and meters. This confines emissions in liquid transfer operations primarily to displacement of the atmosphere in the container being filled. For a covered container it should be possible to estimate by engineering calculation what these losses will be. If the container is open (for instance, an uncovered tub), the amount of solvent lost through evaporation will be more difficult to determine. Breathing losses, due to changes in temperature and atmospheric pressure, must also be considered. However, if the turnover of the storage tanks is high compared to the size of the tanks and if the tank is not subject to large short term temperature fluctuations, this breathing loss should be less than the filling losses.

The finished product filling area represents another source. Emissions from this area would normally be part of the building ventilation exhaust. Determination of the quantities involved must depend on operating experience and measurements.

Liquids handled in drum size quantities are subject to evaporative losses during dumping operations. Again these would normally show up in the building ventilation. The potential for emission on a per gallon basis is higher for liquids handled in this form since the dumping tends to cause more agitation of the liquid and tends to be performed into open tanks.

Dry solids handling is a source of particulate emissions. Materials of this sort are usually received in 50 pound bags or in fiberboard drums. Until the bags are opened and dumped no emissions will occur from this source. The bags are usually opened at the station at which they will be used. These include mills, mixers and dispersers in the case of pigments and the resin reactors in the case of acid anhydrides. Particulate emissions will also be part of the building ventilation system.

b. Paint Operations — The production of paint products themselves consists of milling, dispersion and mixing operations. Ball and pebble mills are free of gaseous emissions, except when loading and unloading, since they are completely closed during operation. Sand mills often discharge into open portable tanks. Since such tanks are not equipped with covers and vents, there exists a source of solvent evaporation associated with the operation of the sand mill. Sand mills can be set up to discharge into closed, vented containers. This will reduce evaporative losses. The high speed dispersers sometimes operate in open tanks and provide a source of solvent emissions. Often, however, finishing tanks are equipped with tops and top-mounted agitators. This should serve to reduce emissions from these sources.

Most of the emissions from the paint manufacturing area will tend to be carried out with the ventilation system. Hoods or local ductwork can be used to collect emissions from points within the paint manufacturing area. In other cases, no attempt is made to contain emissions and evaporation is directly to the plant ambient atmosphere. Particulate emissions from this area will be minimal except when loading dry pigment into the equipment.

c. Resin Production — Resin processing represents a major source of emissions for the coating industry.

Fusion cooking is characterized by a continuous sparge of inert gas. Intermittently during the process, the hatch is opened for charging raw materials. During this time the volumetric flow rate, and associated emissions, are increased considerably. The flow rate can increase during charging to better than 100 cfm.

Since there is less inert gas used in solvent cooking, exhaust volumes are small and consist primarily of noncondensibles. As in the fusion process, however, the rates increase during charging of raw materials. Condensers are used on solvent reactors but must be kept warm enough to prevent accumulations of condensed phthalic. It is common practice in the resin industry to maintain a small inert gas flow throughout a solvent cook to avoid the possibility of leaking air into the system.

Thinning is usually done in separate tanks. The resin batch is "dropped" by gravity feed or pumped into a thin tank which is equipped with a condenser to reduce solvent losses. In some cases thinning is done in the resin kettle itself. This usually results in a higher solvent emission.

2. Raw Materials

The particular raw materials used in a given plant influence greatly both the type and quantity of emissions produced. Emissions potential consists of two problem areas: (a) particulate and (b) gaseous.

a. Particulate — Pigments and extenders account for a major portion of the particulate emissions. The extenders, along with TiO_2, represent the major groups of pigments. Others which find use include iron oxides and carbon blacks. Representative particle size ranges for these products were given earlier in Table 29. Particles outside these ranges are found, but the majority of particles of a particular pigment material, as manufactured, fall within the ranges given.

Some pigments are now available already dispersed as a liquid slurry. The use of this type of raw material will significantly reduce particulate emissions.

The other source of particulate emission consists of phthalic anhydride, PE, or other acids and polyols. This is connected solely with the resin production operation, particularly during, and immediately after charging. This type of emission can be reduced by the use of liquid phthalic anhydride. Sublimed PA can also result in a particulate emission in that the vapor may condense into a fine fume as it leaves the high temperature sections of the equipment. Phthalic also has the unfortunate tendency to plug and foul condensers and similar equipment.

b. Gaseous Emissions — The primary source of gaseous emissions is the solvents. These are potential air pollutants in all phases of the operations including handling, storage, resin production and dispersion and mixing. Basic parameters influencing emissions of solvents include vapor pressure and molecular weight. The rate of evaporation can also depend on such things as diffusivity, surface tension and heat of vaporization. The influence of these properties is less, however, and is rather difficult to predict. Table 26 gives vapor pressures and molecular weights for some of the more common types of solvents encountered in the industry. The molecular weight is important in that it affects the quantity of emissions on a weight basis.

Oils and glycerine are relatively non-volatile and so do not contribute significantly to quantities emitted except at very high temperature. They can, however, be the source of reaction by-products which can present odor problems even in small quantities, or the source of aerosol mists.

3. Start-up and Shut Down

Start-up operations should present no unusual problems provided the appropriate condensers, fans, scrubbers, etc., are turned on at or near the beginning of the process. If the process heat and purge gas is allowed to commence operation before these items are turned on, a significant pollution problem could exist during start-up. It is assumed that kettles, etc., would be purged with inert gas prior to addition of any volatile material.

Shut down operations, particularly if done under emergency conditions, offer a greater potential for air pollution. Good practice would dictate purging lines and vessels with inert gas to eliminate residual solvent and PA. These materials would in all likelihood be vented to the atmosphere. A complete shut down might also involve solvent transfer operations with associated displacement losses.

Shut down of resin reactor in many cases is accomplished by blowing the reactor materials into the thinning tank. This is done by pressuring the tank with inert gas. This inert gas becomes saturated with solvent and must eventually be vented to the atmosphere through the reactor vent or thinning tank vents. This normally results in a highly concentrated emission for a short period.

4. Operation Above and Below Capacity

Aside from the obvious statement that emissions are roughly proportional to production output, operation at other than rated capacity should, in itself, offer no unique problems. Productivity increases are accomplished primarily by increasing the number of batches. Since equipment is sized on a per batch basis, the plant should operate smoothly.

The potential problem areas would more likely involve employee diligence in adhering to proper procedures. As productivity is increased beyond normal levels there might be a tendency for plant housekeeping and control to become sloppy. Operation significantly below capacity might present the temptation to cut operating costs by turning down the operation of scrubbers, etc. The effectiveness of supervision and management will determine the extent to which emissions are adversely affected by production changes.

5. Process Operation Upsets

Several events can occur which could have an adverse effect on emissions. Loss of power would cause a shut down of pumps, stirring devices, controllers, etc. If the dowtherm heater is at a higher elevation than the reactors, a pump will be required to return condensate to the heater. Consequently, fail safe devices must activate which shut off heat to the reactors to prevent accumulation of condensate. Condenser water flow will continue while the scrubber-ejector will cease to function. The inert gas generator will shut down; though the inert gas storage tank will provide a continued supply of sparge gas for a short length of time. The plant will revert to a "status quo" situation in which air pollution effects should be small.

If power is returned soon enough it will be possible to resume operations at the point of interruption. It may be desirable initially to increase the sparge rate in a fusion process reactor until water which has accumulated is removed. Likewise, a period of sparging of the solvent process reactor may be required for the same purpose. For some interval of time after power is resumed, an increase in the emission rate may be observed due to increased sparging.

Condenser failure (due to loss of cooling water, leaks, or other causes) would have unfavorable consequences. The reactor vent would have to remain open until the reactor had cooled sufficiently to lower the solvent vapor pressure to a safe value. Even if the sparge gas is turned off immediately, a considerable amount of solvent would be lost. It is likely that the batch would be lost. It is likely that the batch would have to be cooled immediately with cold dowtherm and, unless there is reason to believe that condenser operation will resume soon, dropped to the thin tank. If condenser failure is on the reactor condenser only, this should result in minimum emission. If, however, there is a general loss of cooling water to the plant there seems no way to avoid a significant emission problem whether the emissions came from the kettle or from the thin tank. Partial failure of condenser (due to fouling, improperly operating controls, or other causes) is common. Often processing is continued in spite of this with a significant increase in emission levels.

Finally, there are several other upsets which can occur to the detrement of air quality. Any upset which results in a higher than anticipated temperature (e.g., failure of temperature controller, improper charging of reactants, etc.) will tend to increase emissions. Any increase in sparging rate will tend to increase emissions. Use of inert gas pressure to force resin from the reactor into the thin tank (e.g., if the transfer line is tending to plug) will cause increased emissions. As discussed earlier, when the last of the resin comes through, the pressure in the reactor will be released through the thin tank condenser vent causing a surge in the amount of solvent vapors emitted from the thin tank.

E. Raw Data Tabulated

1. Questionnaires — Emission data has been reported by some of the plants responding to the industry questionnaire that was distributed to a sampling of the industry. The data for those plants having reasonably complete emission inventories is summarized in Tables 38 to 40.

There is wide diversity in the manner in which the data has been submitted. The numbers as reported are difficult to interpret or compare as they stand. It is felt that the only meaningful presentation of the data is to relate total emission rate to production. Emission data by itself contains limited information unless the production rate is also known. This correlation will be presented in Chapter 4.

The tabulation of emission rates do provide an indication of possible non-compliance (depending on local regulations) by some plants. Also, it suggests the range of values that might be encountered in source testing.

One of the paint industries more persistent problems has always been odor nuisance complaints. Data on this subject has also been reported in the questionnaires. Of 76 Type 1 plants, 15 reported odor complaints from residential areas and six from commercial areas. Of the 39 Type 3 plants, nine reported complaints from residential sections. None of the Type 2 plants reported odor nuisance complaints. This information is tabulated in Table 41.

The detection and measurement of odors is a very difficult area to predict. The odor levels around a plant depend not only on the types and quantities of odorants emitted but also on local atmospheric conditions, presence of competing odor sources, and proximity of neighboring residential or commercial areas. Ultimately, subjective criterion must be relied upon.

The information reported by the questionnaire sample suggests that resin processing represents the primary odor problem. This may be due to the presence of high temperatures which tends to produce small quantities of particularly noxious substances.

Industry source test results have been listed in various parts of this report where it was deemed most appropriate. Test results were obtained by air pollution control equipment manufacturers as well as paint and resin producers. Information on reactor emissions can be found in Section II-C-2 of Chapter 1. Information on performance of control equipment can be found in Section IV of Chapter 5. Test results obtained by the Federal EPA can be found in Section II-G of Chapter 1 and in Appendix D.

F. By-Products

The only reaction by-product present in any quantity is water formed in the esterification reaction by which alkyds are produced at about 4 to 5% by weight of the final resin product solids.

TABLE 38

EMISSION DATA FROM QUESTIONNAIRES

PAINT AND RESIN PLANTS

Organic Vapors		Particulates	Plant Size*	
From Paint Production	From Resin Production		Solvent Base (MM Gal)	Resin (MM Lb)
46 lb/day			0.4	—
2.3 lb/hr	1.1 lb/hr	8.4 lb/hr	2.2	6.7
108,000 lb/yr	5,600 lb/yr		4.9	10.0
46 lb/hr			2.0	—
31 lb/hr	15.9 lb/hr		3.3	72.2
27 lb/hr	18 lb/batch		3.8	—
		15 gr/SCF @ 18,000 SCFM	—	—
24,500 lb/yr	11,000 lb/yr		0.6	0.5
400 lb/day	100 lb/day		1.9	4.8

*Based on 16 hr day and 6 day week

TABLE 39

EMISSION DATA FROM QUESTIONNAIRES

PAINT PLANTS

Organic	Particulate	Plant Size*, MM Gal
5.4 lb/hr		3.1
2.09 lb/hr		0.5
8.94 lb/hr		0.6
30.0 lb/hr		3.3
23,650 lb/yr		0.2
1,300 gal/yr		0.1
2 lb/hr		1.3
10 lb/hr		0.4
	183 ton/yr	—
3,425 gal/yr		0.3
4 lb/hr		2.2
5 lb/hr		0.2
48.9 lb/hr		15.4
	8.7 gr/SCF @ 800 SCFM	—
	2.78 lb/hr	—
68,000 lb/yr		2.7
248 lb/day		1.7

*Plant size represent solvent based production only and is based on 16 Hr operating day — 6 day work week

TABLE 40

EMISSION DATA FROM QUESTIONNAIRES

RESIN PLANTS

Organic Emissions	Plant Size* (MM Lb)
360 lb/hr	20.5
2 lb/hr	3.8
3 lb/hr	8.6
8.7 lb/hr	25.5
15 lb/hr	3.6
1.27 lb/hr	39.1
66.6 lb/hr	21.7
3.3 lb/hr	14.7
4.5 lb/hr	1.8
24 lb/hr	11.7
7 lb/hr	10.3
39.1 ton/yr	4.0
15.7 lb/hr	60.3
668 lb/hr**	47.0

*Based on 16 hour day — six day week

**Most of this emission is from "Resin Dryers"

TABLE 41

QUESTIONNAIRE SUMMARY OF WASTE MATERIAL DISPOSAL

		Production Data			Solvent and Water Usage for Clean Up					
		Coatings 10^5 gal/yr		Resin & Varnish 10^5 lb/yr	Waste Solvent 10^5 gal/yr		Waste H_2O 10^5 gal/yr		Waste Resin	Waste Paint
Type	Number	Solvent	H_2O	(NVM)	Kettles	Other	Kettles	Other	10^5 lb/yr	10^5 gal/yr
1	76	1,261.37	483.22	5,303.90	8.57	30.54	16.34	130.34	15.96	9.52
2	209	905.97	413.19	–	–	18.06	–	33.49	0.81	1.49
3	39	–	–	6,398.57	2.34	1.29	43.45	253.95	24.08	–
Total	324	2,167.34	896.41	11,702.47	10.91	49.89	59.79	417.78	40.85	11.01

ODOR COMPLAINTS FROM QUESTIONNAIRES

		Odor Nuisance Complaints	
Type plant	Number of Plants	Residential	Commercial
Paint & resin	76	15	6
Paint only	223	0	0
Resin only	39	9	0

In addition to water, various reaction by-products are formed in very small quantities. Often these are detectable only by very sensitive analytical procedures. These products are important, nevertheless, in that they constitute a primary source of odor problems even when present in minimal quantities. These substances include aldehydes, esters and organic acids.

1. Liquid Wastes — Waste materials constitute a major source of potential liquid pollutants. These include spoiled batches, residues and solvent and aqueous solutions for washing equipment. The industry questionnaires have provided a source of information on this subject.

The questionnaires requested information on the amounts of resin and of paint disposed of as well as solvent and water usage for clean up. The results have been tabulated and are given in Table 41. Note that even plants which produce no water based coatings reported use of aqueous solutions (probably caustic) for washing purposes. It would not be entirely accurate, then, to assign all the aqueous waste to water based paint production. Nor, in the case of Type 1 plants, is it possible to assign the portion of waste which is attributable to paint production as opposed to resin production. It is apparent from the questionnaires that the term "kettle" means different things to different people. To some, "kettle" is reserved for resin and varnish cooking vessels while in other cases mixing and finishing tanks are also included in the term. One cannot necessarily assign washing solutions for kettles to resin production in the case of Type 1 plants. Some generalizations can be made:

a. Aqueous waste far exceeds solvent wastes for all types of plants.
b. The major portion of solvent wastes can probably be attributed to coating production as such.
c. Waste resin and paint account for less than 0.5% of shipments.

2. Solid Waste — Most solid waste, with the exception of that which can be considered part of an air pollution emission, is incorporated into the liquid wastes described in the previous section. These include pigment particulate and latex emulsion as well as the non-volatile portion of the film former which would be left if the paint or resin were allowed to dry.

G. EPA Source Test Data

The U. S. Environmental Protection Agency retained Scott Research Laboratories, Plumsteadville, Pa., to source test several resin kettles. Flow rates, total hydrocarbons and gas chromatography data were obtained from several processes. The test methods used are described in Chapter 3, Section I-C. The results are presented in Appendix D. Portions of this section have been taken from the report prepared by Scott Laboratories for the E.P.A.

A summary of the batches tested follows:

Three basic types of varnish cooks were tested. These consisted of a polyester fusion cook, an alkyd-fusion (oil modified polyester) cook, and an alkyd-solvent cook. In addition, some thinning operations were tested. A detailed description of each process tested is given below.

Linseed Soya Alkyd Fusion Cook

This alkyd resin is a long oil alkyd produced from linseed oil, soybean oil, pentaerythritol, and molten phthalic anhydride.

The two oils were added to the kettle and heating began. After the oils were added, a blanket of inert gas was maintained over the batch. When the oils had heated sufficiently, the pentaerytritol (PE) was added. The steam ejector was turned on in order to create a vacuum in the stack while the PE was being dumped from bags into the reactor porthole. The temperature was raised and a liquid catalyst was added. The batch was then heated to 440°F and kept at this temperature until samples of the batch passed a clear test (test used to indicate completion of reaction). The temperature was then reduced and molten phthalic anhydride was added. The batch was reheated to 460°F; upon reaching 460°F, the inert gas blanket was removed and 20 SCFM of inert gas was blown into the batch from the bottom of the kettle. This inert gas blow-through aids in removing water produced in the process reaction. The inert gas flow as increased to 30 SCFM and maintained until the proper acid value and viscosity were measured. Samples were obtained by opening a porthole and removing some resin by means of a dipper. The 30 SCFM inert gas blow was removed and a 5 to 10 SCFM blanket of inert gas maintained while the resin was cooled to 425°F. The batch was then dropped into a thinning tank containing solvent.

A description of Kettle 4 may be found in Appendix D, Figure D-1.

Soya Alkyd-Fusion Cook

This alkyd resin is a medium oil alkyd produced from soybean oil, pentaerythritol (PE), and molten phthalic anhydride. The oil was heated and then part of the PE added. A clear test was run and then the remainder of the PE and molten phthalic anhydride was added. The steam ejector was on only during the time that PE was being loaded into the reactor. A 5 to 8 SCFM inert gas blanket was maintained during the initial period of heating and loading the reactor. A 10 SCFM inert gas blow was started when the cook reached 480°F and was increased to 20 SCFM during the last part of the cook. Resin was cooled to 430°F and dropped into solvent.

TABLE 42

SUMMARY OF TESTED BATCHES

Process Type	Kettle Number	Run Number	Total Cook Time (hrs)	Pounds of Resin Produced	THC Mass Emissions lb/ton Resin	Max. Emission Rate lb/hr
Alkyd Fusion (linseed-soya)	4	1	13	5500	—	—
Alkyd Fusion (linseed-soya)	4	2	12	5500	1.10	0.70
Alkyd Fusion (linseed-soya)	4	3	12.5	5480	2.94	2.80
Alkyd Fusion (soya)	3	1	12	5300	0.43	0.54
Alkyd Fusion (soya)	3	2	15	5350	0.52	0.64
Alkyd Solvent	2	3	16	24030	0.31	1.07
Alkyd Solvent	2	1	21.5	24000	0.048	0.004
Alkyd Solvent (abort run)	2	2			—	—
Polyester Resin	8	1	18	6787	12.42	5.95
Polyester Resin	8	2	18	6506	12.78	9.75

A description of reactor number three is also shown on Figure D-1* since reactors three and four are identical.

Soya Alkyd-Solvent Cook

This resin is considered a long to medium oil alkyd made from soybean oil, pentaerythritol, crotonic acid, and phthalic anhydride; it is used as a major ingredient in producing an acrylic resin. Soybean oil, pentaerythritol and crotonic acid were placed into the reactor with the steam ejector turned on; fumes were vented out the main stack (A) during this time. Upon completion of loading, the ejector was turned off and a 10 SCFM blanket of inert gas was maintained over the batch while it was heating. Upon reaching temperature molten phthalic anhydride was added, the main stack was closed, and the kettle sealed. Xylene was added and the inert gas flow turned off. The condenser was turned on and the batch was heated so that the solvent and water (reaction product) began refluxing. During this period of the process the emissions were vented from the receiving tank stack (B). The water driven off the kettle was drained from the receiving tank several times during the cook; the solvent was returned to the batch. After the cook was completed, the batch was cooled to 400°F and dropped into an empty thinning tank.

A description of reactor number two and associated equipment is presented in Figure D-2.*

Polyester Cook

This resin is a saturated polyester produced from propylene glycol, butylene glycol, glycerine, and dimethyl terephthalate (DMT). This resin is used in producing powder coatings. The use of DMT to fulfill the acid functionality results in the evolution of methanol rather than water as a reaction product. The steam ejector was turned on while the raw materials were being added. During this time emissions were vented to the main stack "A". The solvent was then added and the reactor was sealed. Heating of the batch was begun; fumes were vented from stack "B" during this time. As the temperature increased distillation began. The temperature was then held constant. When the amount of distillate coming off decreased considerably, a 10 CFM inert gas blowthrough was begun to step up the reaction.

All of the distillate collected in the receiver tank was drained into drums. When the reaction stopped, the batch was placed under a vacuum. During this time all emissions to the atmosphere were vented to stack "C". The batch was left under vacuum until the proper viscosity was reached. Upon completion the resin was dropped into 55 gallon drums.

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*Appendix D

A description of reactor eight and its associated equipment is presented in Figure D-3.*

Thinning Operations

With the exception of one case, the thinning operations consisted of dropping the completed resin directly from the reactor into a thinning tank containing the appropriate amount of solvent. In one case, the resin was dropped into an empty tank and then the solvent was added to the resin. In all cases, the emissions to the atmosphere simply consisted of fumes forced out of the tank by positive displacement. All the tank vents were equipped with condensers to reduce emissions. Figures D-1, D-2, and D-3* indicate the thinning tank, condensers and vent locations.

Discussion

The primary difficulty associated with measuring mass emissions from the various fume stacks was the extremely low flow and "breathing" flow situations encountered. For most of the larger stacks (8-9 in. diameters) where the pitot tube and hook gauge were used, the pressure differentials were, in many cases, approaching the minimum sensitivity of the apparatus. In sampling the smaller 2 inch stacks where the bag systems were more easily adapted, more confident data were obtained. Where the "breathing" flow situations occurred, a high degree of care was required to insure that the one-way flow valve was operating properly.

After having experienced the various flow situations associated with this type of process operation, a more sophisticated flow measuring system could probably be engineered for future investigations.

The kettle operator also had a direct effect on the flow rate at certain times during a particular cook. He had control over the quantity and duration of inert gas and steam ejection, and as a result, two different cookers processing similar batches of resin could create dissimilar mass emission rates at the kettle outlet.

The results of the Orsat and chromatographic analyses for oxygen and carbon dioxide in the bag samples yielded a large variation in stack gas molecular weight for the various stack gases sampled. As a result an average molecular weight was determined using the extremes of 28.96 for ambient air and 29.88 for the inert gas stream that was used as a gas blanket in all the process operations. This average molecular weight of 29.42 was used in all stack gas velocity measurements.

All the flowrate averages used to calculate mass emissions are included in Tables D-1 to D-16.*

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*Appendix D

The total hydrocarbon measurements were reasonably complete with the exception of the reflux cycles on polyester resin cook #1 where the heated prefilter was not closed properly and a leak occurred.

Upon examination of the data included in Tables D-1 to D-7*, it can be noted that relatively good comparison exists between the average ppm-C levels for similar modes within process run pairs. A similar comparison involving mass emissions, however, does not yield the same reasonable duplication. The problem exists with the variations in flowrates experienced between similar modes of the process run pairs. Some explanations for these variations have been discussed previously.

Tables D-1 to D-7* describe the process mode breakdown for each cook and includes average flow and mass emission rates for each process mode. The flow and mass emission data for the eight thinning tank tests are presented in Tables D-8 to D-9*.

All gas chromatography traces were reduced by first identifying specific hydrocarbons, where possible, and then measuring peak areas and comparing them to standards. In an effort to condense the data in a more useable form, the specific hydrocarbons were reduced to four main groups: Aliphatics (C_6-C_{10}), Aromatics (C_6-C_8), identified oxygenates, and branched Aliphatics (C_8-C_{12}). The data summaries (Tables D-10 to D-16)* present each process cook sampled with average flow rates, total hydrocarbon emission rates, and the percentage of specific hydrocarbons found in each of the above groups.

A summary of thinning tank emission data is presented in Table D-9* using the same format described previously.

The GC data obtained for the alkyd solvent cooks were a great deal easier to interpret than that of the fusion cooks due to the basic three component makeup of their effluents. One difficulty arose when an attempt was made to compare the total carbon found with the hydrocarbon analyzer, to that found with the gas chromatograph.

Even though the total hydrocarbon analyzer and the gas chromatograph were both adjusted for carbon response, the data did not always coincide. The following sources of error could explain this discrepancy.

1. The total hydrocarbon analyzer gives a continuous plot of the hydrocarbon concentrations, while the G.C. gives only a point sample. With the fluctuating organic concentration, this point sample may or may not be representative of the effluent.
2. Since the nature of the work did not permit duplicate injections into the chromatograph, an

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*Appendix D

injection error, perhaps sample pressurization, could have occurred.

3. The concentration of xylene was so high that even with the .25 cc sample loop, the column was nearly overloaded. This could add another non-linearity aspect to the system.

CHAPTER 2

INDUSTRY STATISTICS

I. TYPE, SIZE AND LOCATION OF PRESENT DAY PLANTS

The Paint and Allied Product Industry (SIC 2851) is made up of approximately 1,727 establishments operated by some 1,365 companies.[7]

These plants and companies primarily manufacture coatings such as paints, varnishes and lacquers, along with such allied products as putty, caulking compounds, cleaners and other paint sundries.

Primary to the Paint Industry are two broad categories of products, generally referred to as "Trade Sales" and "Industrial Finishes".

Trade Sales products are usually "shelf items" to be used on the exterior and interior surfaces of houses and buildings. These are manufactured in a wide range of colors and are usually applied with brushes or rollers, although other application techniques are also employed.

Industrial Finishes are generally produced for and sold to other manufacturers for application to durable customer products. The final application varies from spraying, dipping, etc., to electrostatic methods.

Although some of the smaller manufacturers still tend to specialize in either Trade Sales or Industrial Finish products, this tendency is not as strong as it has been in the past. Most of the larger companies now produce both types.

A breakdown of the industry by product class is provided in Figure 29. The major categories indicated are listed below in order and with product class codes:

(2851) 1. Exterior, oil-type sales paint products.
(2851) 2. Exterior, water-type paint products and tinting bases.
(2851) 3. Interior, oil-type trade sales paint products.
(2851) 4. Interior, water-type paint products and tinting bases.
(2851) 5. Trade sales lacquers.
(2851) 6. Industrial product finishes, except lacquers.

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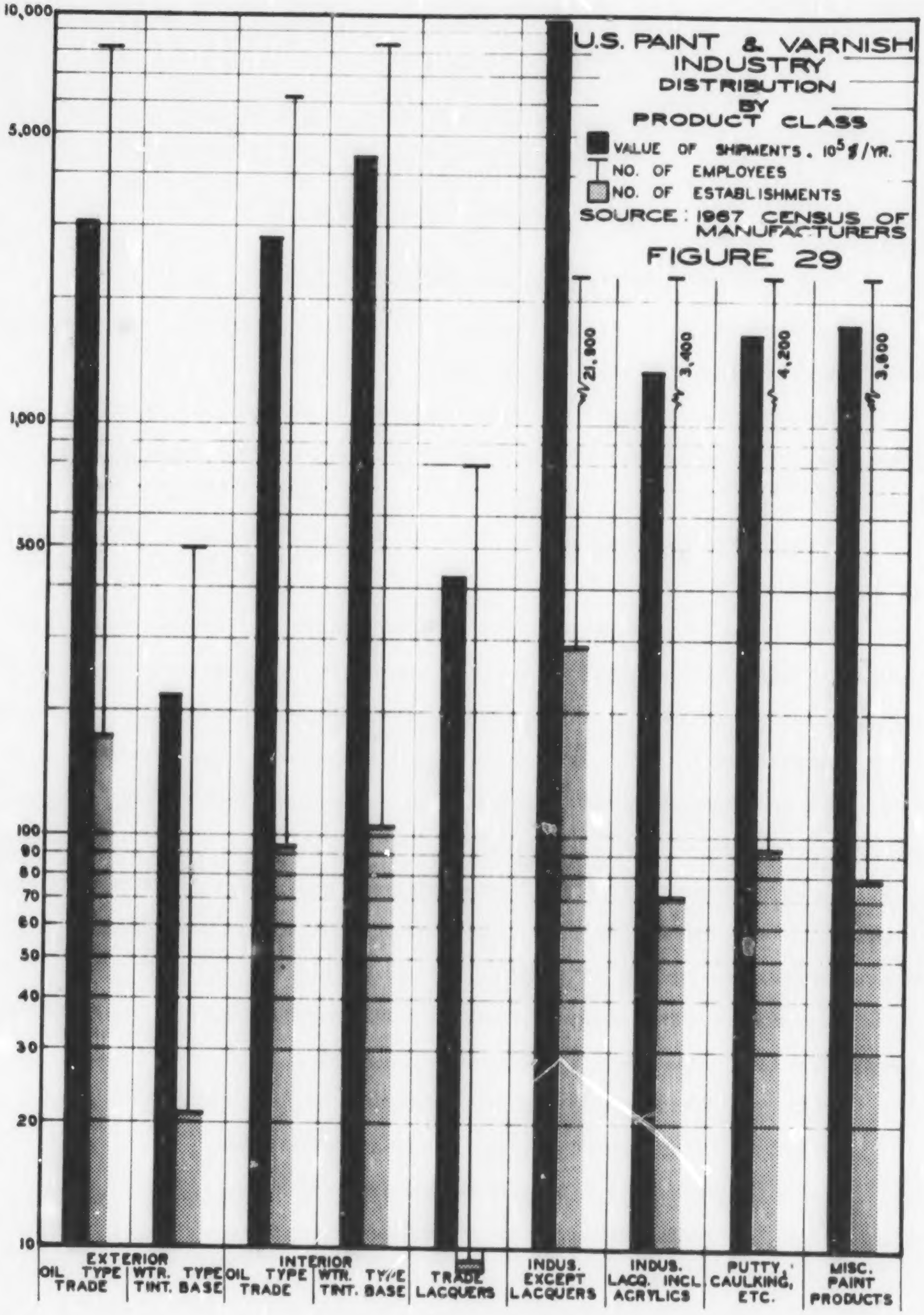


U.S. PAINT & VARNISH INDUSTRY DISTRIBUTION BY PRODUCT CLASS

SOURCE: 1967 CENSUS OF MANUFACTURERS

FIGURE 29

(2851) 7. Industrial lacquers, including acrylics.

(2851) 8. Putty, caulking compounds and allied products.

(2851) 9. Miscellaneous paint products.

This histogram uses abbreviations of the above categories and is a plot of value of shipments, number of establishments and number of employees for each of the (product) classes. Statistics are based on the 1967 Census and no effort has been made to estimate corresponding figures for other years. The number of establishments shown accounts for little more than 50% of the total and provides a distribution of those showing some degree of specialization.

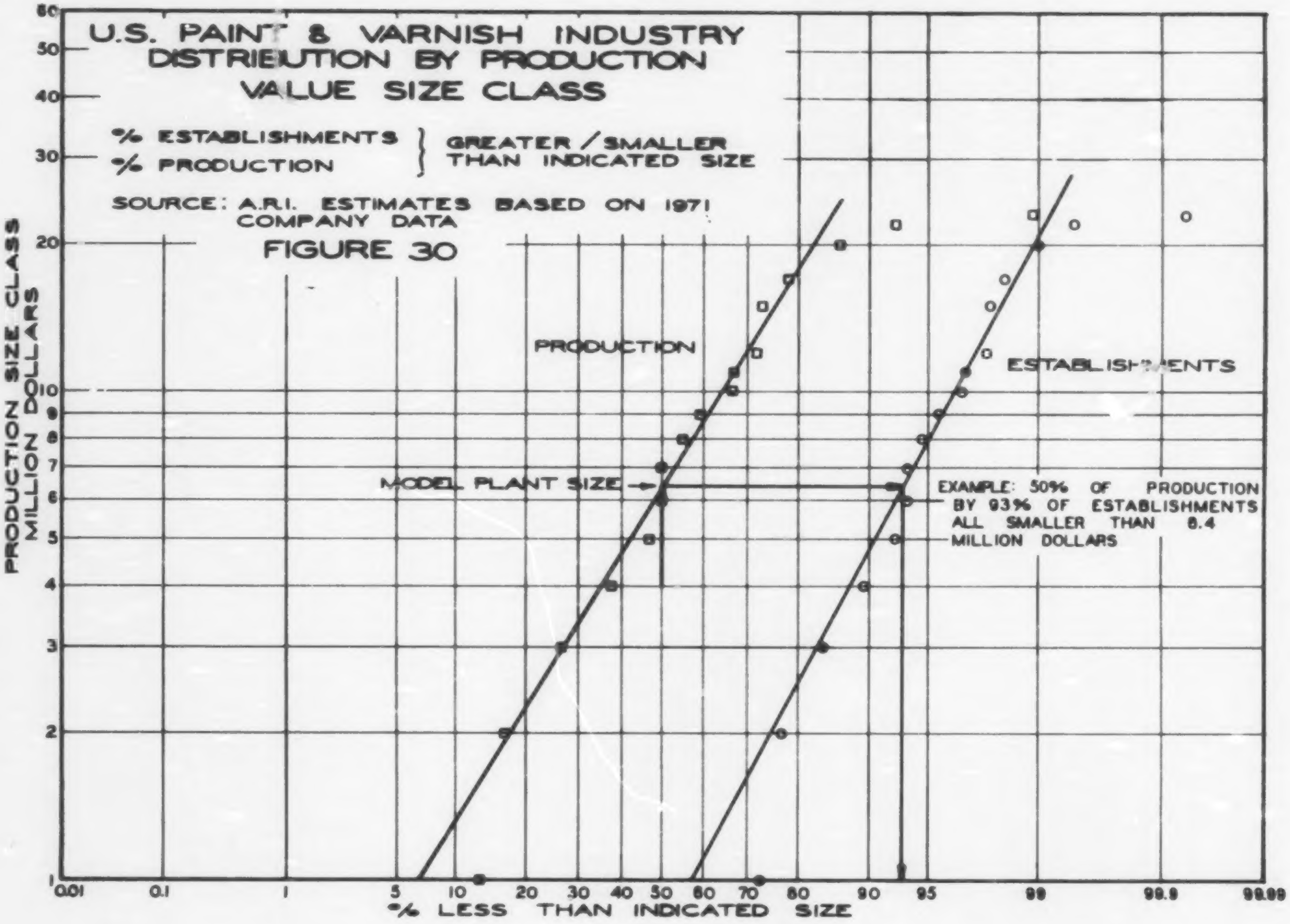
Figure 30 provides a distribution of paint plants by size as measured by production value. It was based on estimates from data for individual companies reported by Kline's *Marketing Guide to the Paint Industry*.[1] This distribution follows the log-probability law rather well and is, consequently, plotted on a probability x 2 log cycle grid. In practice, the small percentage of very large plants show wide variations, partly because data on an individual plant basis is often withheld. In addition, it is common in statistical data of this nature to find that the extreme values do not follow the log-normal distribution.

The example, shown by arrows in Figure 30, illustrates one of the useful aspects of a log-probability plot. At the $6.4 million plant size lies the median production — half the paint is produced by plants smaller than (or larger than) this size. Only 7% of the plants, however, are larger than this size. The median plant produces somewhat less than $1 million worth of product.

It is of interest to note that the Model Plant discussed in Chapter 1 produces product valued at about $6.6 million. This production value level is indicated by an arrow in Figure 30.

Figure 31 provides a distribution of plants and industry employees by plant size as measured by the number of people who work in the plant. It is based on figures taken from *County Business Patterns*.[13] This Bureau of Census publication lists the number of plants in various size ranges such as 1 to 3 employees, 4 to 7 employees, etc. From these tabulations, it is possible to obtain the percentage of plants with fewer than a given number of employees. Figure 31 plots percentage of plants smaller than indicated plant size. The total number of employees in any plant size can also be computed and expressed as a percentage of total employment in the Paint and Varnish Industry. For example, as shown by arrows on Figure 31, 30% of the plants in the industry employ less than 8 people, 30% of the industry employees work in plants that have a plant employee size of less than 50, and this plant size accounts for 78% of the industry plants.

Statistical measures of distribution: median, mean and mode have been included in this

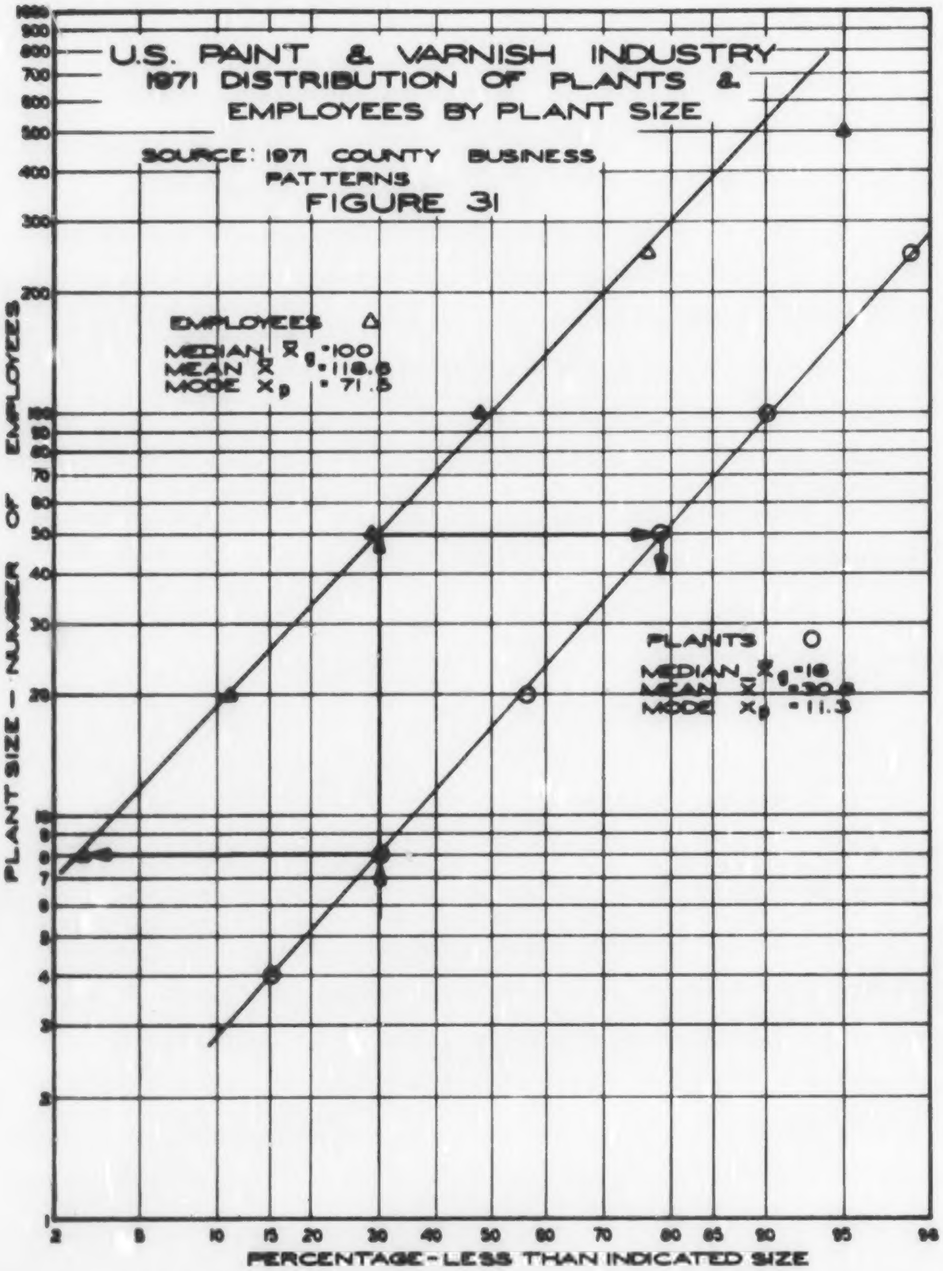


U.S. PAINT & VARNISH INDUSTRY DISTRIBUTION BY PRODUCTION VALUE SIZE CLASS

% ESTABLISHMENTS } GREATER / SMALLER THAN INDICATED SIZE
% PRODUCTION

SOURCE: A.R.I. ESTIMATES BASED ON 1971 COMPANY DATA

FIGURE 30


U.S. PAINT & VARNISH INDUSTRY
1971 DISTRIBUTION OF PLANTS & EMPLOYEES BY PLANT SIZE

SOURCE: 1971 COUNTY BUSINESS PATTERNS

FIGURE 31

figure. These measures were similarly computed for past years and changes in them were used to make projections for future plant sizes. Further discussion on projections will be found in part II of this section under the subtitle "Size of Plants."

Geographical locations of areas of concentrated production are indicated in Figure 32. To arrive at volume production for each state in 1972, state-by-state dollar production figures for 1967 (as reported by the Census of Manufacturers) were converted to gallons using average cost per gallon, as computed from Current Industrial Reports. Computed production growth rates were used to arrive at 1972 production volumes of each state. Since these volume production figures represent a second generation estimate, they are indicated as ranges on the map. Estimated volumes of the eight largest producers are shown in rectangular boxes.

Locations and number of plants by state for 1967 can be found later in Figure 35, a histogram used for making projections in the following section.

II. PAST, PRESENT AND PROJECTED INDUSTRY TRENDS TO 1985

Several references, mostly published by Bureau of the Census, have been employed in computing past and present production and in projecting future levels. Three main sources used are:

1. *Current Industrial Reports*, Series M28F[8]
2. *Census of Manufacturers*, 1967[14]
3. *County Business Patterns*[13]

Various Industrial Reports were used to tally annual productions for 1965 to 1972 (Figures for 1972 are based on estimates for December 1972) in dollar value and gallon volume. Geographical distribution on a state-by-state basis is based on the 1967 Census — the most recent available at time of writing. Distribution of plants by employee size class are based on *County Business Patterns*.

A. Production

Average annual growth of production rates were computed for the seven year base period and applied to years in the 1972 to 1985 period. Projections for these years are plotted in Figure 33 as million gallons, and in Figure 34 as million dollars of shipments per year. Computed average growth rates are indicated in terms of percent of current production per year for Trade Sale Finishes, Industrial Finishes and total sales in each figure. Results are summarized on the following page.

Year	Trade Sales Million Gallons	Trade Sales Million Dollars	Industrial Million Gallons	Industrial Million Dollars	Total Million Gallons	Total Million Dollars
1965	411.0	1247.0	365.0	922.3	776.0	2169.3
1972	456.0	1663.7	474.4	1355.6	930.4	3019.3
1985	550	2845	770	2775	1320	5620
Avg. Annual Rate %	1.50	4.21	3.82	5.66	2.63	4.84

The average growth rate was calculated in a manner similar to compound interest. For example, let A be the production volume for the first year and B the volume for the *nth* year. The average annual growth rate, a, is determined by solving the following equation for a:

$$A\,(1 + a)^n = B$$

For total gallon production, this becomes

$$776.0\,(1 + a)^7 = 930.4$$

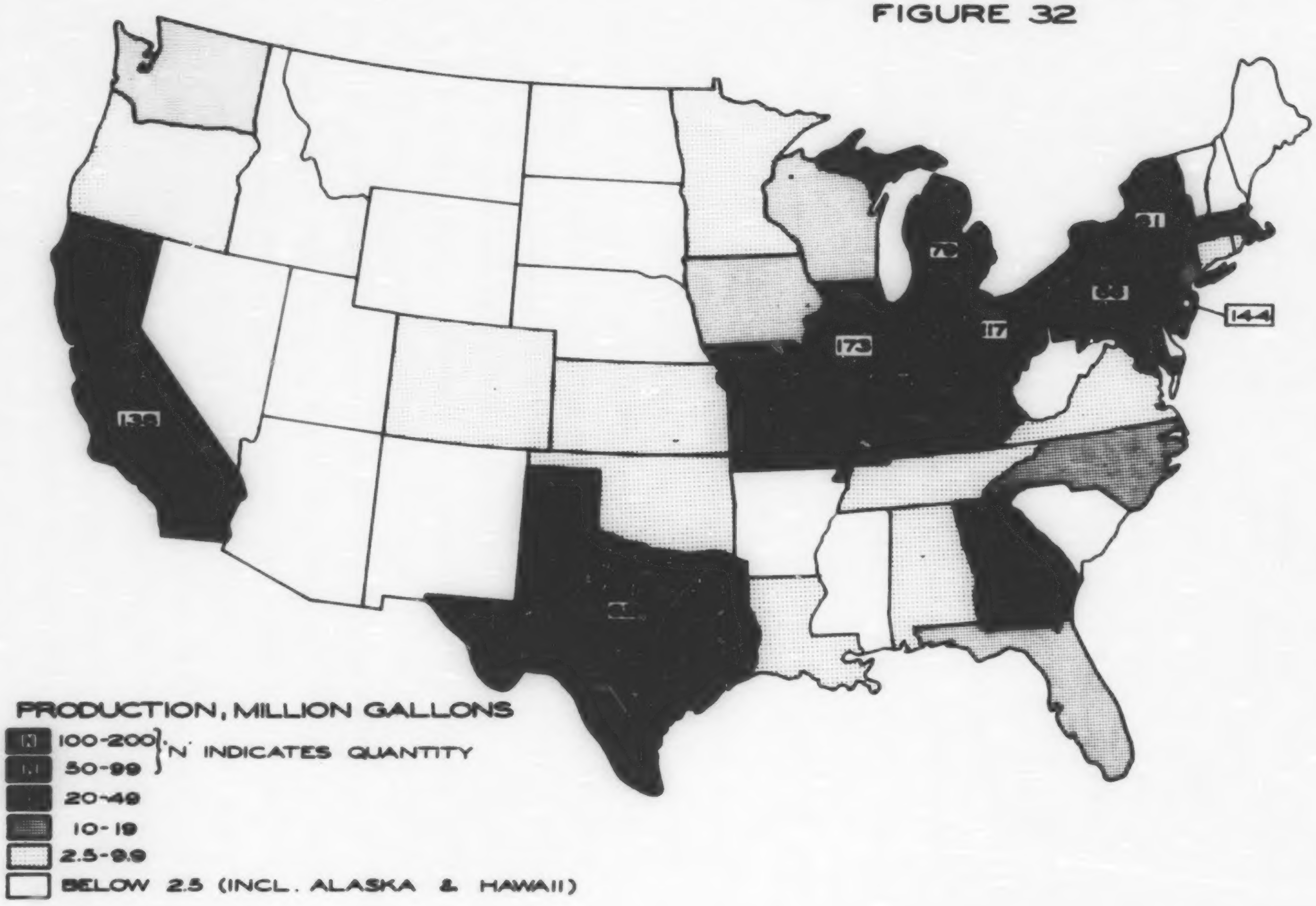
and a = 0.0263. The projected growth curve will plot as a straight line on semi-log coordinates. The line, by definition, will pass through the first and last points.

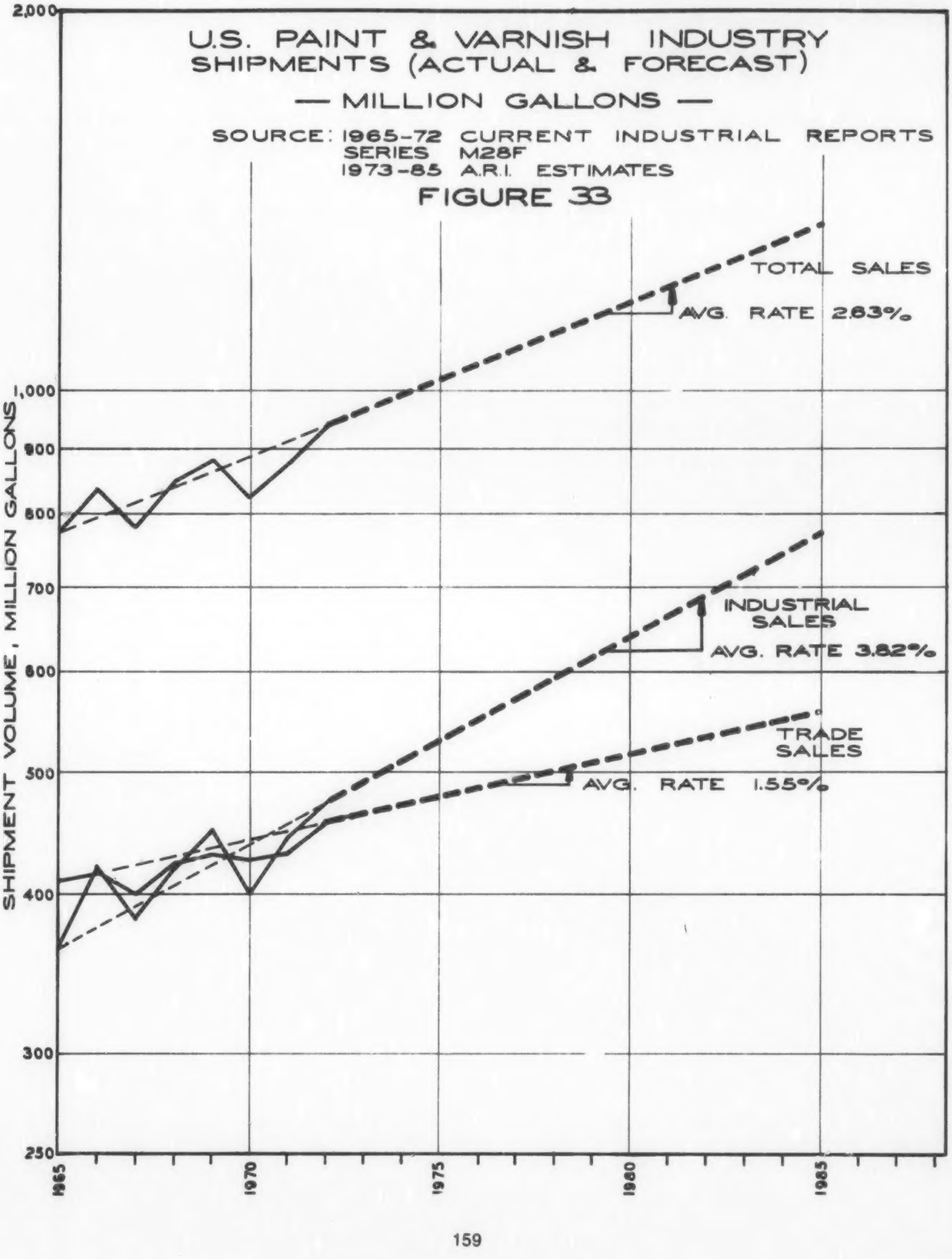
It is apparent from these figures that in 1972 Trade Sale Finishes accounted for 49% of the volume and 55% of the dollar value. In terms of gallons, this compares with 53% in 1965 projected to shrink to 41.5% in two decades. Over the same time period, however, revenues from Trade Sales are expected to register a much smaller drop: from 57.5% of the total in 1965 to 51% in 1985. This comparison is readily apparent in the plots of Figures 33 and 34. The higher growth rates (in terms of both volume and value) for Industrial finishes are attributed to the trend for precoated materials such as siding for houses, paneling and certain plastics. Industrial finishes display higher growth rates than Trade Sales. Their share of the market increases even more dramatically when measured in gallons than in dollar value. This is attributable in part to the lower cost of packaging and transportation required for industrial products.

Total production figures for 1967 as reported in the *Census of Manufacturers* differ from those reported in the *Current Industrial Reports* by about 25% (variations between these sources are somewhat smaller for the census years 1963 and 1958). The *Current Industrial Reports* are published monthly and present a source of up-to-date information. They are estimates from a sampling of about 310 plants and do not represent the accuracy that might be expected from the larger sampling used in the *Census of Manufacturers* reports. Unfortunately, these reports are prepared only about every four years.

U.S. PAINT & VARNISH INDUSTRY
DISTRIBUTION BY STATE
ESTIMATED 1972 PRODUCTION
— MILLION GALLONS —

FIGURE 32



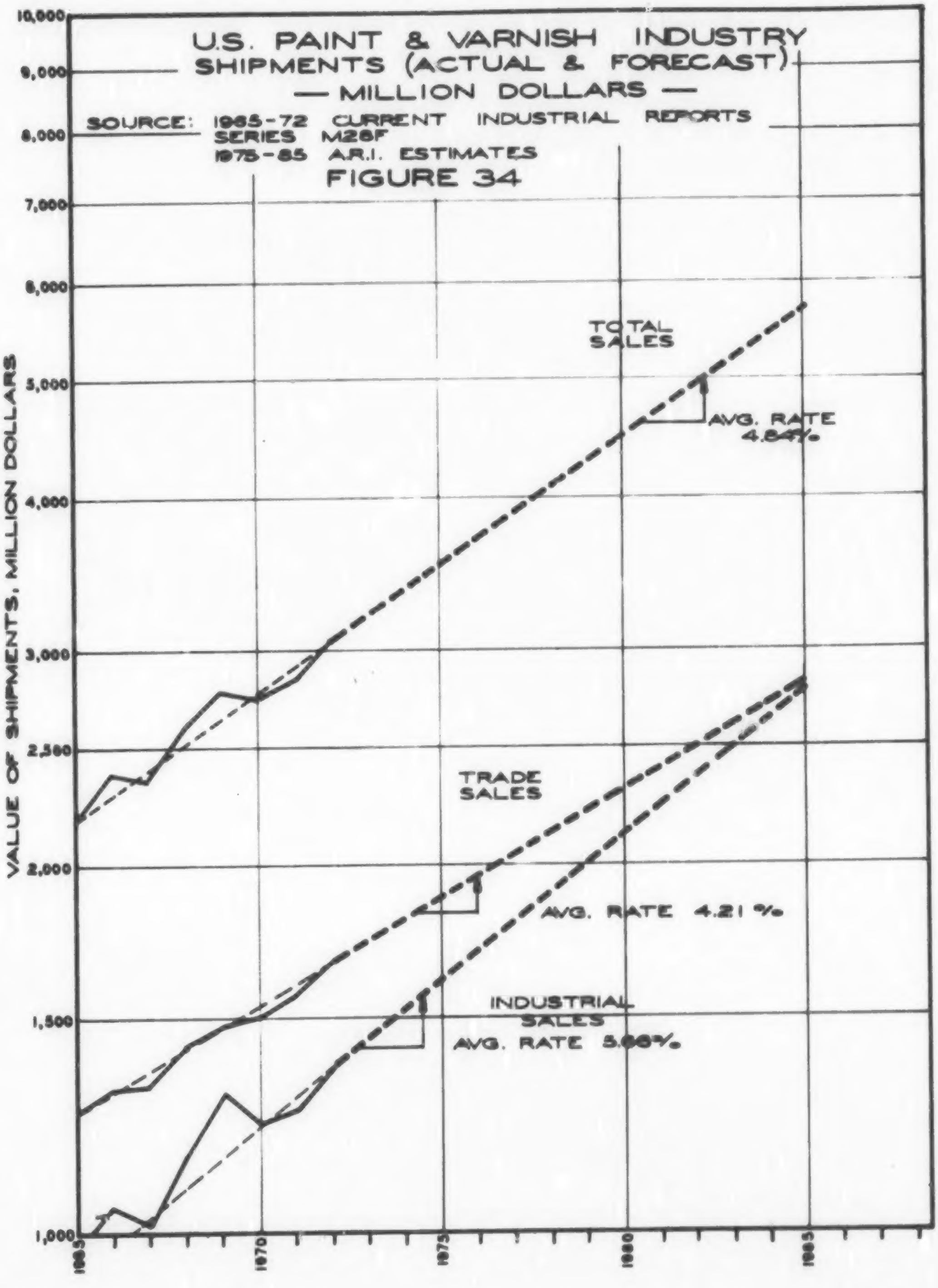


U.S. PAINT & VARNISH INDUSTRY SHIPMENTS (ACTUAL & FORECAST)

— MILLION GALLONS —

SOURCE: 1965-72 CURRENT INDUSTRIAL REPORTS
SERIES M28F
1973-85 A.R.I. ESTIMATES

FIGURE 33



U.S. PAINT & VARNISH INDUSTRY
SHIPMENTS (ACTUAL & FORECAST)
— MILLION DOLLARS —

SOURCE: 1965-72 CURRENT INDUSTRIAL REPORTS
SERIES M28F
1973-85 A.R.I. ESTIMATES

FIGURE 34

Statistics presented by the Census are, nevertheless, the most detailed available and Figure 35 is based on them. This histogram provides a state-by-state breakdown, for 1967, of value of shipments and number of establishments and employees. States with less than $6 million in shipment value are not indicated. Projected values for 1972 and 1985 are also shown for each state; these values are based on growth rates computed from the *Current Industrial Reports*.

It can be assumed that, despite the difference of total production as stated by the two sources, growth rates derived from one can be applied to geographical distribution obtained from the other. The second simplification assumed in estimating 1972 and 1985 productions was that each of the 30 states would increase at the same industry-wide rate. This accounts for equal increments on the logarithmic scale used in Figure 35.

Whereas projections based on average annual growth rates over preceding years do not directly take into account several variables that could affect production (such as projected growth rates of all industry, GNP, population, per capita consumption, technological breakthroughs, etc.), it is expected that a similar number and nature of variables existed and determined output over the base period. Consequently, projections based on increasingly complex and seemingly sophisticated indices may be no better than those obtained above. Factors used here and elsewhere represent, at best, an approximation of future trends.

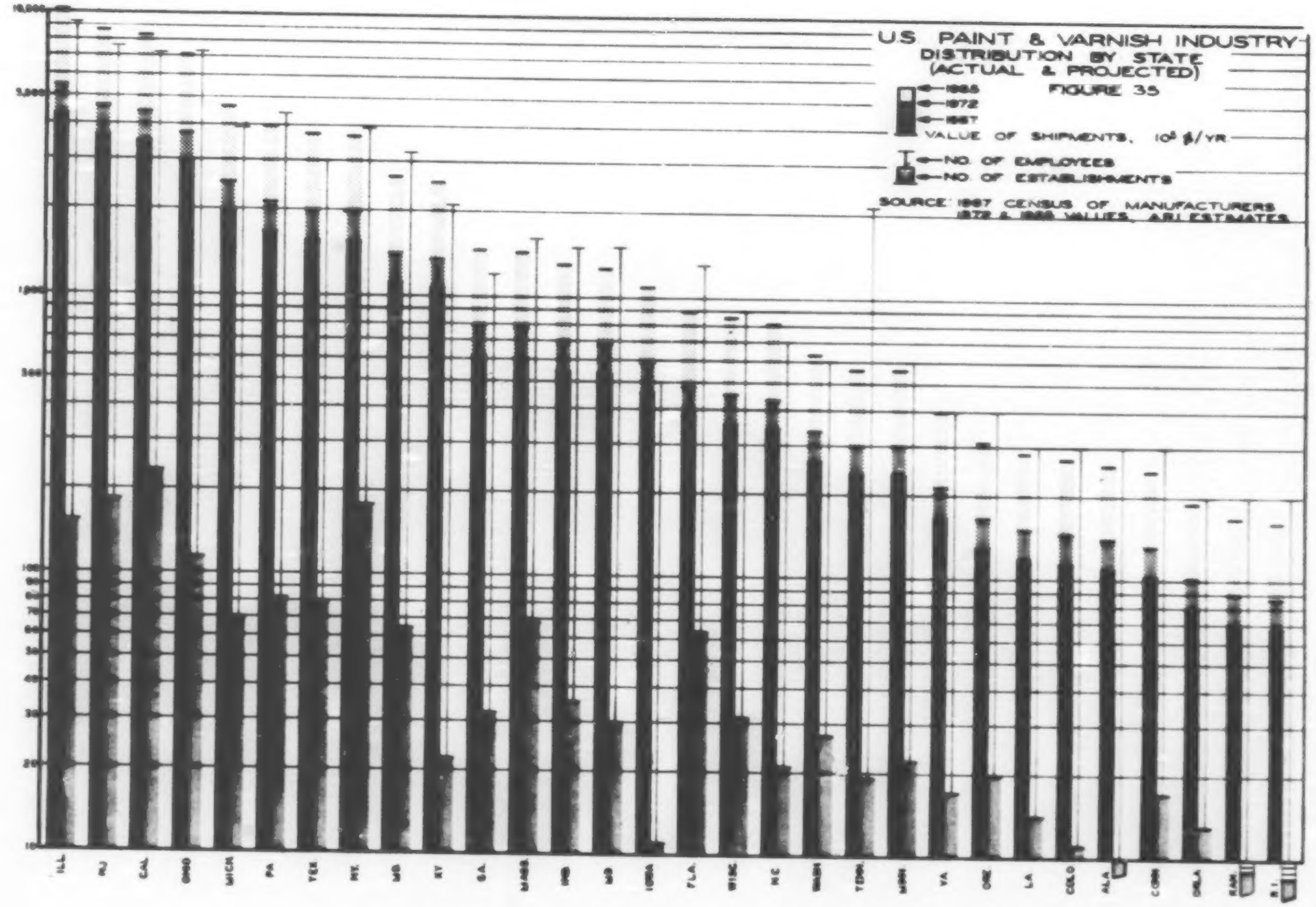
B. Number of Plants

The number and size of the plants operating is somewhat vague, with the *Census of Manufacturers* reports perhaps being the best source of information available. According to the Census reports, the number of plants and companies operating them are shown below:

Year	No. of Plants	No. of Companies	Plants w/20 or More Employees
1958	1,709	N/A	600
1963	1,788	1,579	654
1967	1,701	1,459	680

The number of establishments (plants) is only an approximation because those plants with less than ten employees were not required to complete the census report in 1967, resulting in estimates being calculated and incorporated into the figures. The count on those plants with 20 or more employees is far more reliable.

In terms of geographical location, Figure 35 plots the number of plants for each of the top 30 paint-producing states. There is, apparently, very little direct correlation between paint produced



U.S. PAINT & VARNISH INDUSTRY
DISTRIBUTION BY STATE
(ACTUAL & PROJECTED)
FIGURE 35

SOURCE: 1967 CENSUS OF MANUFACTURERS
1972 & 1985 VALUES, ARI ESTIMATES

and number of plants in a given state indicating emphasis, in some areas, on smaller plants.

C. Size of Plants

As indicated in Figure 31, the median plant, when ranked by number of employees, in 1971 had 16 employees whereas the median employee, ranked by the size of the plant in which he worked, was employed in a plant having 100 employees. This merely implies that 50% of the plants employed more than 16 people, but 50% of industry work force were working in plants having 100 or more workers. The plot provides a quick and easy method for finding the percentage of establishments in any selected size range.

The only plant size projections attempted are in terms of number of employees. As previously discussed in Part I of this chapter, the number of plants in each size category (1 to 3 employees, 4 to 7 employees, etc.) was expressed as a percentage of total plants. These figures were obtained for the years 1965 to 1970 from the *County Business Patterns* of corresponding years. Since successive years shows small changes, the total change was measured in terms of the statistical distribution parameters: geometric standard deviation, mean, median and mode. As illustrated earlier in Figure 31, a log-probability plot of the distribution greatly facilitates computation of these parameters from which a "bell curve" can be derived, if desired.

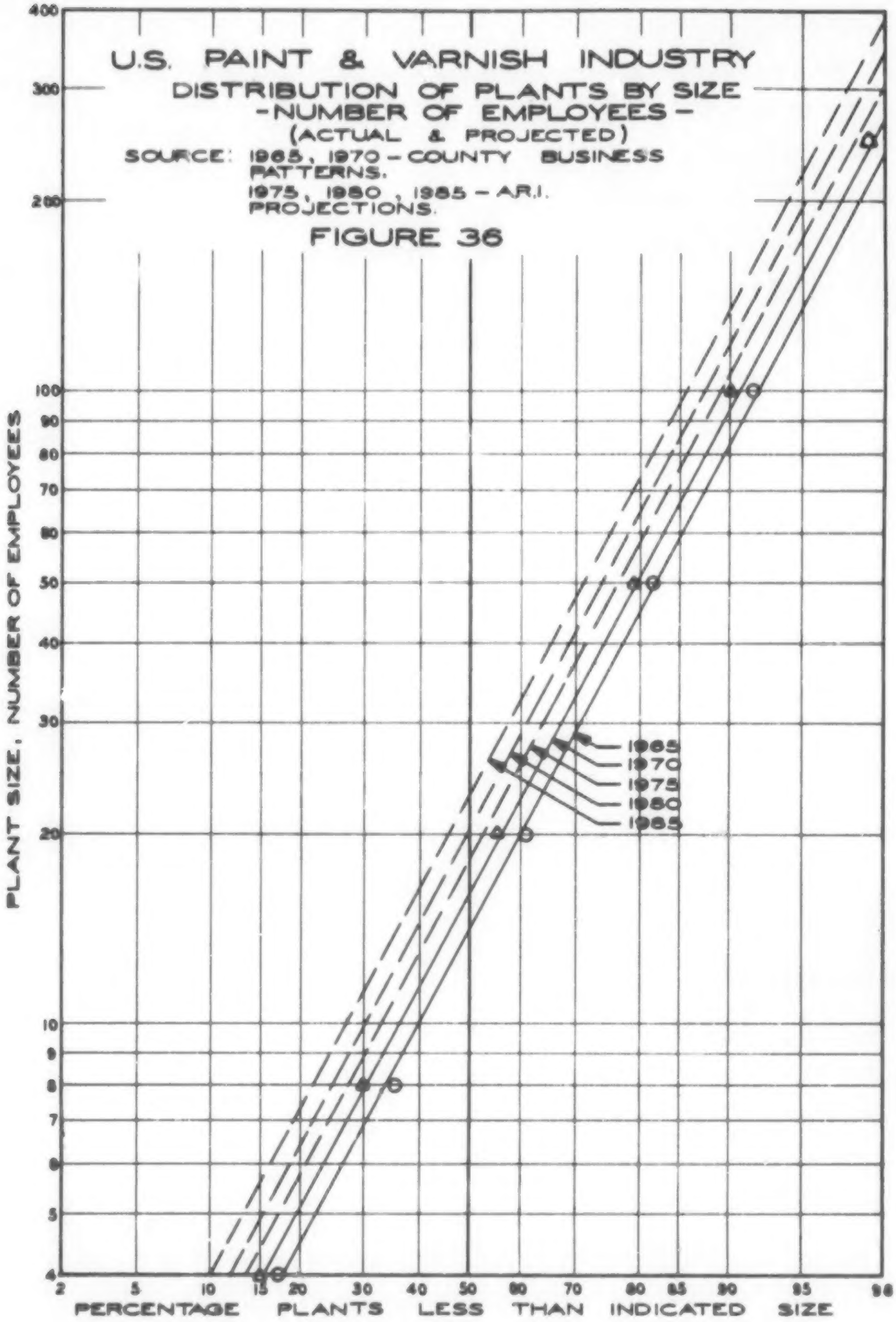
Figure 36 plots percentages of plants smaller than indicated employment size — actual distributions for 1965 and 1970 and projected distributions (broken lines) in five-year increments to 1985. Actual distributions are completely defined by:[21]

1. Geometric mean, or median, which is plant size class at 50%, and
2. Geometric standard deviation which is equal to

$$\frac{\text{plant size class at 84.1\%}}{\text{plant size class at 50\%}}$$

There was found to be a negligible change in the latter quantity over the five-year base period. Had there been a noticeable difference this would have resulted in different "slopes" for 1965 and 1970, and the projected distributions would need to take this into account. Instead, since the plots are "parallel," projections can be based on a change of median size alone.

The increase in median plant size appears minor (16 employees in 1965 to 23 employees twenty years later). At the 98% point, however, Figure 36 indicates that the number of employees will have increased from 230 to almost 400. Conversely, the largest 2% of the plants will have increased in size to employing more than 400. This increase in size is in spite of technological improvements and increased productivity. Table 43 lists percentages of plants in indicated employee



U.S. PAINT & VARNISH INDUSTRY
DISTRIBUTION OF PLANTS BY SIZE
-NUMBER OF EMPLOYEES-
(ACTUAL & PROJECTED)
SOURCE: 1965, 1970 - COUNTY BUSINESS PATTERNS.
1975, 1980, 1985 - A.R.I. PROJECTIONS.

FIGURE 36

TABLE 43

U.S. PAINT AND VARNISH INDUSTRY

DISTRIBUTION OF PLANTS BY EMPLOYEE SIZE CLASS

Percent of Establishments in Indicated Employee Size Class

Year	1971	1970	1969	1968	1967	1966	1965
Employee size Class							
1 to 3	15.2	15.2	15.4	16.3	17.8	17.8	17.9
4 to 7	15.4	15.5	15.8	16.5	15.5	17.4	18.0
8 to 19	26.3	25.1	25.1	25.3	25.7	25.9	25.4
20 to 49	22.0	23.5	23.0	22.2	21.6	20.7	21.3
50 to 99	11.3	11.1	11.1	11.0	11.1	10.2	9.5
100 to 249	7.3	7.1	6.6	6.3	5.9	5.6	5.7
250 to 499	2.1	2.3	2.5	2.0	1.9	2.0	1.7
500+	0.4	0.3	0.5	0.5	0.6	0.4	0.5
Total units reporting	1,568	1,597	1,607	1,624	1,654	1,690	1,734
Total employees	63,865	65,601	66,474	63,623	64,959	62,359	63,255

Source: "County Business Patterns", U.S. Summaries for 1971, 1970, 1969, 1968, 1967, 1966 and 1965 size classes. It is noteworthy that the total number of plants has registered a decline for every year from 1965 through 1971.

This increase in average size is not surprising since the paint industry is labor intensive. It is not feasible to operate on a continuous production basis as in chemical manufacturing. Larger equipment can be used to increase batch size and productivity, but the wide range of products and colors still precludes the use of any other technique except batch processing.

In Figure 35 a comparison between the bar indicating number of plants and the line giving number of employees will yield an average plant size for each state.

D. Capacity — Production Relations

There are no statistics available on theoretical capacity for the industry. One can "pick" a reasonable number, such as 80% or 90% and assume that all plants, on an average, operate their equipment at this fraction of full capacity. If necessary, one could calculate industry capacity by dividing production data previously presented by 0.80 to 0.90.

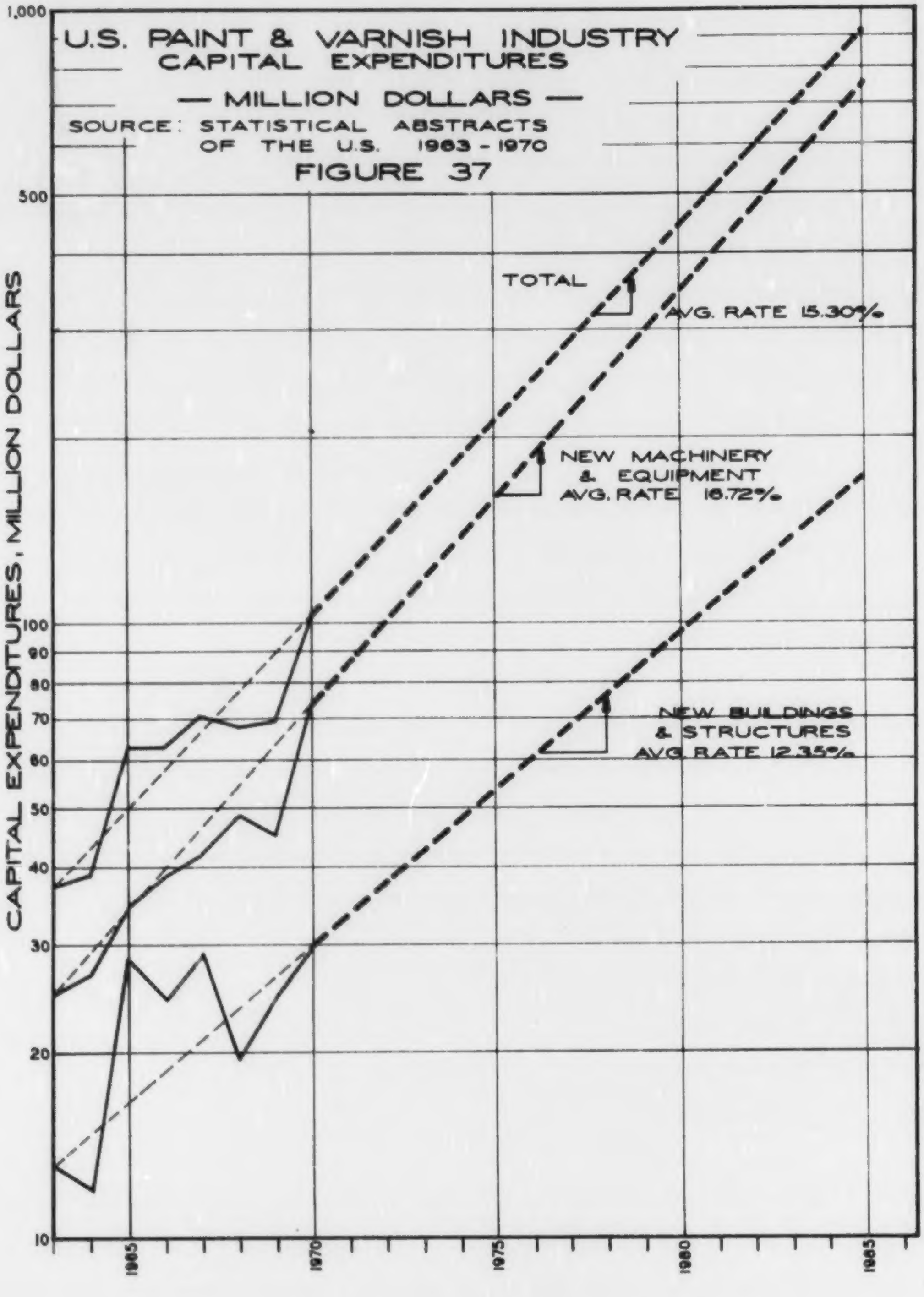
E. Typical Plant and Equipment Ages

It is suspected that a vast majority of the some 1,700 establishments will have quite old structures and equipment. There are several reasons for arriving at this conclusion:

1. To avoid high shipping cost, most of the plants are established in geographical sections of the country where the paint demand is high (see Figure 32).
2. Most have been established for quite a number of years, having evolved from single ownership to corporate structure in these geographical areas where land values and construction cost have increased at a very rapid pace.
3. Paint manufacturing does not cause extensive damage to buildings, nor does it have a deteriorating effect on a majority of the equipment used.
4. Inspection of capital expenditures (see Figure 37 and the accompanying discussion on capital expenditure, Section III) shows us that for the period of 1963 to 1970 an average of 35% has been expended for buildings and structures, while 65% has gone for new machinery and equipment.

Within the Paint Industry the following types of equipment will be found:

1. Storage tanks
2. Reaction kettles
3. Pumps and motors
4. Filters and strainers



U.S. PAINT & VARNISH INDUSTRY
CAPITAL EXPENDITURES
— MILLION DOLLARS —
SOURCE: STATISTICAL ABSTRACTS
OF THE U.S. 1963 - 1970
FIGURE 37

5. Filling and capping equipment
6. Packaging equipment
7. Mixing and dispersing machinery
8. Grinding machinery
9. Electronic instruments of various types
10. Material handling equipment.

Much of this type of equipment is common to other industries and requires little change to adapt to paint manufacturing.

In general, we would expect to find quite old structures, many of which may be 50 years old or older. However, the equipment should be relatively newer due to changes in manufacturing and increasing batch size. The average age of equipment may run in the range of ten to twenty years.

F. Technological Revolutions and Outside Influences Causing Changes in the Industry

The paint and varnish industry as a whole is not a large investor in research and development. Less than 10% of the research and development dollar goes for basic research. The vast majority goes for the support of existing products, solution of manufacturing difficulties, and customer assistance. Certain selected areas of research are being intensively studied, however. These are discussed below.

Many of the smaller firms cannot afford sizable research and development expenditures and depend upon raw material suppliers and group research firms who pool their efforts for the member companies. The most prominent group research firms are the Paint Research Association in Chicago and the Coatings Research Group in Cleveland.

1. Application Techniques — Perhaps the most dynamic changes in the industry are being brought about by advances in the state-of-the-art; advances which could well be termed technological breakthroughs, in retrospect, if current developmental work is successful and results in wide acceptance. Such advances include:

1. Powder coatings
2. Electrostatic spray
3. Electrodeposition
4. Radiation curing

Powdered coatings represent one significant advancement, in recent years, for the industry. In addition to its several technical advantages this method eliminates the use of solvents, thereby reducing atmospheric pollution as well as fire hazards at points of production and application.

Although some powders present a dust explosion hazard, this problem can be taken into account during design of the process.

It is expected that the industry will concentrate much attention on development and use of powder coatings. Powder coatings can be applied with flocking guns, electrostatic spray equipment, or electrostatic fluidizing chambers. The best known method uses a preheated object immersed into a fluidized chamber where the powder is kept in motion by ascending gas flow. Powder coming in contact with the preheated surface melts and fuses to the surface. The coating is cured in an oven. A patent was recently issued to Grow Chemical Company covering the production of powder coatings in water slurry form. It is said that these can be applied with existing solvent based equipment.[22]

Much recent interest in this field has been expressed by automobile manufacturers who claim that recycling permits material utilization of 98%.[23] Ford has been powder coating truck wheels for a few months and is expected to announce in late 1973 a pilot line for applying topcoats. General Motors has a one-color automatic spray and recovery unit for topcoats. This unit employs eight guns.

Estimates for powder coating consumption range as high as 200 million pounds/year for metal coating by 1980. In addition, the powder coating of glass containers is said by some to offer an equal potential consumption by 1979,[24] for a total of 400 million pounds per year by 1980. These estimates are admittedly somewhat optimistic but more stringent air pollution regulations could tip the scales in their direction.

Electrostatic forces have been employed in spraying methods. Basically, a charged (paint) particle will follow an electric field. If an electrical potential difference exists between a particle and a surface, the particle will tend to flow to the surface and be deposited there. Various available methods differ only in the method whereby the particles are charged and brought to the proximity of a surface. Any material loss occurs only for those particles whose momentum in a direction away from the piece to be coated overcome the electrostatic force of attraction. A reduction of spraying velocity will, therefore, minimize losses.

Electrodeposition differs from the above in that electric forces are used to deposit liquid paint particles much like in an electroplating operation. The coating material contains resins, additives and pigments. Complete and uniform coverage of all exposed surfaces can be obtained. Film thickness is uniform since the deposition ceases when the film is thick enough to act as an insulator at the applied voltage. Materials used are generally water-based thus reducing solvents.

Radiation curing utilizes free radicals and ions to initiate polymerization or other reactions required for a complete cure. A thin beam of electrons is generated by applying 300 kilo-volts to a high vacuum accelerator tube; this beam can be used for curing with very little heat build-up making it particularly desirable for coating wood, rubber and fabric materials. Although this method is suitable for continuous curing its use has been curtailed by high costs and technical problems. Ultraviolet and high intensity visible radiation have also been utilized for curing.

2. Pigment Industry — Another important area where technology is expected to set the trend is in the pigment industry, in the production of titanium dioxide. Estimates[25] indicate that the production by the chloride process will surpass that using the sulfate process by 1975. Currently the chloride process accounts for about 47% of the production, its share is expected to grow to 60% while total production advances by 18%. Listed below are estimates for totals of seven leading producers of the pigment:

	MM lbs		
Process	Current	1975	1973*
Sulfate	918	818	737
Chloride	820	1,230	837
Total	1,738	2,048	1,574

The sulfate process uses a lower grade, iron containing, ore known as ilmenite or high TiO_2 slag. The ore is dissolved in concentrated sulfuric acid to form sulfates of both iron and titanium, and titanium dioxide is precipitated as a hydrate. The chloride process, on the other hand, starts with Rutile, a high grade ore or upgraded ilmenite. Technology for using ilmenite directly has recently been developed by duPont.[26] Also, anatase production by the chloride process is presently under investigation. The sulfate process results in a significant potential for emissions of sulfur oxides. The chloride process is inherently cleaner. It not only has a lower potential contribution to air pollution but also has fewer liquid wastes.

Foreign trade is generally not expected to be a major factor in the coatings industry. However, imports have been increasing recently for titanium dioxide with a significant increase in 1972. Aided by the general economic upturn in industry that year, demand so far outstripped supply of TiO_2 that suppliers reduced inventories by more than 50% of the previous year. Imports of this vital pigment almost doubled, with West Germany and Canada providing most of the difference (75% of the increase over 1971 and 48% of the total imports in 1972).

While demand grew, domestic production remained essentially static. Two leading suppliers

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*E. I. duPont estimate

Air pollution legislation has also had its effect on the Paint Industry, particularly those regulations patterned after "Rule 66" which seeks to control the emissions of photochemically reactive hydrocarbons which react with nitric oxide in the presence of ultraviolet radiation to form oxidants.

The Water Pollution Control Act as amended in 1965 and 1972 has, and will cause many paint manufacturers to design alternate ways of discharging waters. The industry contributes to water pollution primarily through the discharge of slurries.

III. DISTRIBUTION OF CAPITAL EXPENDITURES

The Paint and Varnish Industry has shown a fairly steady increase in capital expenditures over the 1963 to 1970 period. Figure 37 is a plot of expenditures for new buildings and structures and for new machinery and equipment. Totals are also plotted for the seven-year period. Although this industry does not spend as large a percentage of its revenues in this category as does the entire Chemical Industry, it has maintained a steady input of funds in response to growing demands. Since 1963, approximately 65% of all capital expenditures have been for new machinery and equipment with the remainder going for new buildings and structures.

Average annual growth rates for capital spending were computed for the base period, for each category, and for the total. These rates were used in projecting to 1985. The rate for total spending averages 15.3% — a rate that seems unrealistically high, especially when compared to the rate of increase in value of shipments. This is further emphasized by selecting the six-year base period 1963 to 1969 which reduces the growth rate substantially resulting in capital expenditures less than 50% of those obtained by using the 1963 to 1970 period (to illustrate, the reader may draw an imaginary line through the corresponding points for 1963 and 1969 and extend this line to 1985). This apparent discrepancy seems unavoidable where data is subject to very large year to year fluctuations as in the case here.

While Figure 37 attempts to provide a long range picture of the capital spending pattern, Table 44 provides a comprehensive distribution of labor and finance within the industry. Statistics here include a listing for Inorganic Pigments.

TABLE 44

U.S. PAINT, VARNISH AND INORGANIC PIGMENTS INDUSTRY

1967 LABOR AND FINANCE SUMMARY

		Paint & Allied Products	Inorganic Pigments
		1,701	98
Establishments	Total	1,701	98
Establishments with 1 to 19 Employees		1,021	38
Establishments with 20 to 99 Employees		521	33
Establishments with > 100 Employees		159	27
Employees	Total	66,100	12,600
Payroll	Millions of Dollars	492	97.2
Production Workers		36,300	8,900
Wages	Millions of Dollars	223.4	63.2
Man Hours	Millions of Hours	73.1	17.7
% Man Hours	January to March	24.2	26.0
% Man Hours	April to June	25.45	25.4
% Man Hours	July to September	25.5	23.7
% Man Hours	October to December	24.9	24.9
Cost of Material	Millions of Dollars		
	Total	1,606.4	235.0
Materials, Containers, etc., Consumed		1,461.0	197.3
Cost of Resales		125.9	15.2
Fuels Consumed		7.8	15.4
Purchased Electricity		9.8	6.3
Contract Work		1.9	0.9
Value of Shipments	(Including Resales)	2,911.4	549.3
Value of Resales		173.2	20.1
Value Added by Manufacture		1,318.5	316.3
Manufacturers Inventories	Millions of Dollars		
Beginning 1967	Total	406.1	104.3
Finished Products		224.8	45.0
Work in Process		23.9	9.6
Material, Suppliers, Fuel, etc.		157.4	49.7

TABLE 44 (continued)

U.S. PAINT, VARNISH AND INORGANIC PIGMENTS INDUSTRY

1967 LABOR AND FINANCE SUMMARY

		Paint & Allied Products	Inorganic Pigments
End of 1967	Total	426.7	108.6
Finished Products		234.6	
Work in Process		27.7	9.6
Material, Supplies, Fuel, etc.		164.4	51.9
Expenditures for Plant and Equipment		73.5	21.7
New Plant and Equipment Total		70.7	20.8
New Structures and Additions to Plants		28.8	3.1
New Machinery and Equipment		41.9	17.7
Used Plant and Equipment		2.8	0.9

Source: 1967 Census of Manufacturers, Bureau of the Census

CHAPTER 3

MEASUREMENTS OF EMISSIONS

I. SAMPLING AND ANALYTICAL PROCEDURES

A. General Requirements for Source Testing

Several comments can be made concerning source testing for the Paint and Varnish Industry.

1. The testing personnel should become as familiar as possible with the process under investigation *before* testing begins. Products produced, raw materials used, conditions of operation, location of sampling points, etc., should be ascertained as much as possible.

2. The chemical identity of the probable emissions species should be anticipated in advance and their chemical and physical properties determined. A brief description of the species that may be encountered in various types of operations follows.

Some of the emissions characteristics of resin and varnish cooks are covered in Chapter 1. The major part of the emissions from these operations consists of solvents, steam, and some of the more volatile reactants. Also present will be various reaction and degradation products that can be formed during processing such as aldehydes and organic acid. The latter products are usually present in relatively small amounts. However, they often constitute the most noxious components of the fumes. Table 45 lists the more common raw materials and solvents used in the manufacture of various resins. This list is not intended to be comprehensive, but should be used only as a guide as to what to expect when source testing a particular resin operation.

Since thinning is sometimes done in the resin cooker, solvents can represent a major emission even from fusion processing. The properties of the solvents used should be kept in mind when designing an analysis train for source testing. The chemical composition and vapor pressure characteristics are of particular importance. The boiling range of selected solvents is given in Table 46. A boiling *range* is given even for specific compounds since the grades usually used in the paint industry are of varying degrees of purity.

TABLE 45

COMMON RAW MATERIALS AND SOLVENTS USED IN THE MANUFACTURE OF RESINS

Resin	Raw Materials	Solvents
Alkyd	Polybasic Acids	Xylene
	Phthalic Anhydride	Mineral Spirits
	Maleic Anhydride	Toluene
	Fumaric Acid	Naphtha
	Polyols	
	Glycerol	
	Pentaerythritol	
	Oils	
	Soya	
	Tall Oil Fatty Acids	
	Benzoic Acid	
Urethane	Toluene Diisocyanate	Xylene
	Polypropylene Glycol	Mineral Spirits
	Linseed Oil	MEK
		Ethyl Acetate
Acrylic (solution)	Acrylic Monomers	Aromatic Hydrocarbons
	Methacyrlic Monomers	Ketones
		Esters
Phenolic	Formaldehyde	Alcohols
	Phenols	Ketones
	Cresol	Esters
Vinyl (solution)	Vinyl Monomers	Ketones
		Aromatic Hydrocarbons
Amino	Dimethylol Urea	Butanol
	Urea	Xylene
	Formaldehyde	
	Butanol	
	Melamine	

TABLE 46

SOLVENT BOILING RANGES

Solvent	Boiling Range, °F
Hexanes	140 to 160
Naphtha (light)	205 to 250
Xylene	275 to 290
Toluene	230 to 232
VMP Naphtha	210 to 300
Regular Mineral Spirits	310 to 395
Aromatics (medium)	315 to 390
Ethyl Alcohol	170 to 174
n-Butyl Alcohol	241 to 246
Acetone	133 to 135
Ethyl Acetate	162 to 176
Methyl Ethyl Ketone	172 to 178
Ethylene Glycol Monoethyl Ether	270 to 279

Source: Martens[4]

In addition to the raw materials and solvents, the source tester should be aware of the possible side reactions that may occur in processing. Certain of these reaction products have a very low odor threshold and their presence in even very low concentrations may be undesirable. For example, polyols can undergo oxidation or dehydrogenation to form aldehydes and ketones. These can undergo further oxidation to acids. The breaking of the carbon chain can occur on oxidation to give an aldehyde and ketone each of which has fewer carbon atoms than the original alcohol. Some of these reactions may occur in the kettle while others may require more severe conditions such as would be encountered in a fume incinerator.

3. The sampling team should have the capability to perform continuous, on-line measurements as well as discrete sampling. The highly cyclical emission curves of such operations as resin cooking makes continuous measurements virtually mandatory.

4. Cross checking of the measurements should be made whenever possible. This should preferably be through on-site analysis to minimize the necessity of return trips. Wherever feasible, an over-all material balance on the sample should be used to check the consistency of the analytical results.

5. Equipment used should be as simple and as portable as possible and require a minimum of utility hook-ups.

6. Explosion proof equipment is required when in close proximity to volatile hydrocarbons.

7. A complete log should be made, if possible, correlating emissions levels with kettle temperature, addition of raw materials and solvents, etc.

B. Description of Source Sampling and Analytical Procedures

1. Flow Measurement — The most widely accepted technique presently consists of flow measurement per ASTM/PTC-27 using a reverse pitot tube (S type). Care must be exercised to see that a representative traverse is made and that the measurement points are sufficiently far from any flow disturbances. Duct temperature and pressure should also be recorded.

Pitot tubes, however, cannot be used with much accuracy below linear gas velocities of 10 to 15 feet/second. For lower gas velocities, various types of anemometers are available including vane, hot-wire, swinging vane and heated thermocouple types. These instruments often have limitations as to the types of environments in which they can be used so care should be exercised in selecting them. Hot-wire types may present an explosion hazard in some atmospheres.

Resin kettle vents are sometimes quite small in diameter (four inches or less). For small diameter vents, the use of a pitot tube can be undesirable in that its very presence in the vent may disturb the flow pattern so as to give a faulty reading. This problem can be overcome in some cases by the use of very small L shaped pitot tubes. These, however, are more prone to clog by, for instance, phthalic anhydride.

An alternate method of measuring low flows in small ducts is through the use of a calibrated orifice. These have been used with some degree of success in the field. A low pressure drop, pre-calibrated orifice is mounted in an assembly which can then be fitted to the end of a reactor vent. All of the gas flow is made to pass through the orifice.

A variation on this scheme, which has met with less success, is the use of a plastic bag provided with a hole. The bag is slipped over the end of a vent and the pressure in the bag during gas flow is measured and correlated with gas flow.

For very low flow situations, the use of a bag without an orifice can be used. A completely evacuated bag can be slipped over the end of the vent and allowed to fill with the effluent gas. In this case, the bag collects *all* of the gas emitted. The bag can then be sealed and the contents pumped out through a meter. The total quantity of gas is then recorded.

A further complication, particularly in resin cooking, is flow rate fluctuation. For instance, when the kettle is opened for raw materials addition, a vacuum is drawn in the kettle causing large volumes of air to pass through the open port, into the kettle, and through the vent. Likewise sparging rate may vary during a cook. If a measure of the total quantity of emissions is to be obtained, flow rate as well as emissions concentration must be known at all times during the process cycle.

For some ducts, such as those associated with baghouses, a pitot tube is suitable. For any device which measures linear gas velocity, the flow profile across the duct should be known at all times. This is often impractical, however, in many process situations. A useful compromise might be to take a traverse during a period of constant flow and monitor the centerline velocity continuously during the rest of the run. If the velocity profile is well shaped, and if the Reynolds' number does not pass through the transistion region between laminar and turbulent flow during velocity fluctuations, then the centerline velocity can be related to the average velocity with reasonable accuracy. In extreme cases, it may be necessary to continuously monitor the velocity at more than one point.

2. Particulate Measurements

a. General Considerations — Here again, considerable variations will be encountered in the amount and nature of particulate emissions. Some of the situations which may be encountered are listed below.

1. Solid, inorganic particulate — An example of this type is pigment particulate. These are essentially non-volatile and have little, or no, solubility in pure water. This type is the easiest to handle from a collection standpoint.

2. Liquid organic aerosol — This represents a more difficult situation. The aerosol will usually be present in a gas stream which is saturated in the vapor phase with the same hydrocarbons present in the liquid droplets. The amount and composition of the aerosol may vary with location. When the gas stream leaves the process unit it is at high temperature and only small amounts of entrained liquid should be present; whereas downstream where the temperature is lower, significantly more may have formed.

The physical properties of some aerosols can significantly complicate source sampling techniques. Where very high boiling components are involved, if the sampling is done by one of the common methods of drying and weighing the collected material, the aerosol will be included in the total particulate measurement. Where a more volatile aerosol has been collected, it may evaporate before weighing and be lost. The intermediate situation is more troublesome in that part may be lost and part retained.

3. Solid organic particulate — A good example of this type is phthalic particulate. Some of the same comments apply here that were stated in the preceding case. The organic particulate may be volatile under conditions of subsequent sample processing.

4. Organic vapor — This can be a relatively easy situation to handle providing that the vapor is kept above its dew point in the sampling equipment. Problems can arise due to the large number of chemical species that may be present in a given sample.

b. Collection and Analysis Techniques — The usual procedure for particulate sampling is to sample a portion of the effluent over a period of time using some kind of sampling train. Instantaneous, or "grab" samples, are not well suited to particulate collection. The sampling train consists of a sampling probe, collection device or devices, gas flow meter and a gas pump for drawing the sample.

Sampling of streams containing particulate should always be done "isokinetically" whenever possible. That is, the gas velocity in the probe tip should be the same as that in the bulk gas stream in the vicinity of the sample point. In the case of very small particles, say 5 microns or less, some deviation from isokinetic sampling conditions is acceptable.

Sampling under unsteady state conditions presents special problems. A given stream may be in an unsteady state with respect to flow rate, particulate loading, or both. If the flow rate fluctuates, gas velocity in the vicinity of the probe tip must be monitored and corrections made to the sample flow rate as necessary to maintain isokinetic conditions. If particulate loading changes, then samples must be taken at several times in the process cycle. Unsteady state conditions can be expected to occur often in the Paint and Varnish Industry.

A particulate sampling train in use by the EPA is described in the Federal Register (Vol. 36, No. 247, Dec. 23, 1971). A sketch of the sampling train is presented in Figure 38. The probe and filter holder are heated to prevent unwanted condensation. The first two impingers are filled with water, while the third is left empty and the fourth is filled with pre-weighed silica gel. Details of the operation of this train may be found in the Federal Register referenced above.

The Los Angeles Air Pollution Control District Source Test Manual describes an apparatus similar to the EPA train. The major exceptions are that a small cyclone is placed before the filter and three impingers are used instead of four.

A third alternative is to place the filter holder assembly into the stack itself. In this way, condensation on the filter is avoided since the filter temperature will tend to approach that of the gas stream. This technique also reduces the amount of particulate that could settle on the surfaces of tubing between the probe tip and the filter. This can be particularly important in the case of sticky particulate material.

All of the above methods work well on dry inorganic particulate such as pigment dust. When sticky or tarry material is measured, all methods are subject to problems of clogging in the probe and filter, and deposition of material in the lines. In such cases, it is sometimes helpful to pass the gas sample into the impingers first with the filter placed downstream (but *before* the silica gel). with a volatile solvent, evaporating to dryness and weighing the residue. The disadvantage here weighing the residue. Material deposited in lines can sometimes be collected by washing the lines with a volatile solvent, evaporating to dryness, and weighing the residue. The disadvantage here is that it is not possible to distinguish between aerosol at stack conditions and other condensible materials.

3. Hydrocarbon Analysis

a. Discontinuous Sampling — Included under this classification are any samples drawn over an interval of time comprising only a portion of the process cycle and analyzed on a batch basis to give an average concentration for that time interval. For instance, "grab" samples taken instantaneously as well as semicontinuous samples drawn at constant flow rate for a specified period of time (on the order of 20 to 30 minutes) are considered in this section.

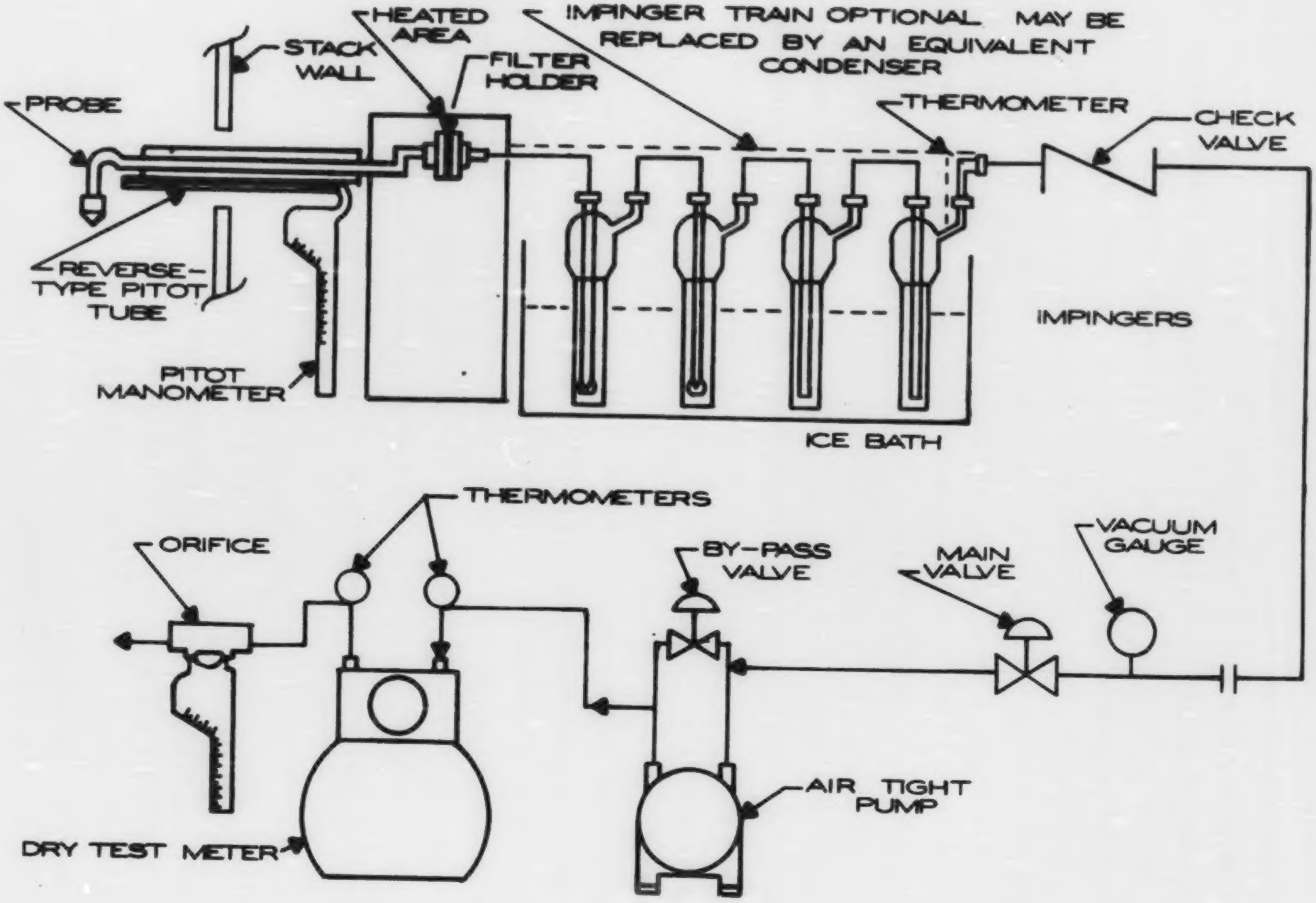

FIGURE 38

PARTICULATE-SAMPLING TRAIN

1. Los Angeles County APCD Methods — The Los Angeles County APCD manual describes several methods of total hydrocarbon analysis. Each method utilizes the same sampling technique which consists of "grab" sampling in evacuated containers. If fitted with an orifice or other control device, the evacuated container can be used to draw semicontinuous samples. Two* liter round bottomed flasks are the containers normally used. Protective wrapping should be applied to minimize breakage where glass containers are used.

Prior to evacuation, the container should be thoroughly cleaned and dried. The sampling line should be equipped with a filter to exclude particulate and provided with a means of flushing with stack gas prior to sampling.

The advantage of this technique is that samples can be taken very quickly. In principal, it is possible to draw a sufficient number of samples over a period of time to catch fairly rapid fluctuations in concentration. For a typical resin cook, however, the number of samples required may be unwieldy.

Potential problems with this approach include clogging of the inlet components, deposition by condensation or adsorption on the walls of the container, and the inability to obtain results in the field. These difficulties make this method unsuitable for testing the effluent from alkyd type cooks and, in fact, the LAAPCD does not recommend it for this type of process. It may, nevertheless, be useful for processes which do not produce high boiling organics, particulates, or aerosols.

Various approaches can be used to minimize, at least partially, some of the objections. Dilution of the sample can eliminate dew point problems in some cases. Adsorption can be minimized by using teflon bags. Heated syringes are available for "grab" sampling. Used with sample dilution techniques these can provide good accuracy and reproducability. Analysis of the sample can be by infrared, combustion analysis, flame ionization techniques, chromatographic, or combinations of these.

2. Semicontinuous Sampling Trains — The Graphic Arts Technical Foundation has devised a method for sampling hydrocarbon emissions in the printing industry. The sample is drawn by an evacuated cylinder through a cold trap immersed in dry ice. This separates the hydrocarbons into "condensible" and "noncondensible" fractions which are then analyzed separately. The noncondensibles in the cylinder are analyzed using gas chromatographic techniques on a Poropak Q column. The contents of the cold trap are analyzed by heating the trap at a controlled rate and analyzing the vapors with a flame ionization detector. If the sample line is heated up to the cold trap and fitted with a filter, this technique should work reasonably well. Its chief disadvantages are

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*Currently using 8 liters

the time required for analysis and the inability to analyze the samples in the field.

Another variation involves collection of a "condensible" fraction in ice water impingers accompanied by continuous, on site measure of noncondensibles using a portable flame ionization detector. The condensibles are measured in the laboratory by evaporating the water and weighing the residue. This is subject to error in some situations due to loss of some of the samples during drying. An alternative to evaporating the water is solvent extraction of the organics in the impingers followed by fractional distillation to remove the solvent. The condensible organics can be further characterized in the laboratory by chromatographic or other means.

Deposition of phthalic or heavy organics in the lines upstream from the impingers can be a problem with this technique. Also, the use of a FID in the field can be difficult and cumbersome.

4. Analytical Techniques

a. Infrared Analyzers — Infrared analyzers are well suited to continuous measurements. Normally, they are set up to monitor a single component. This is the source of their chief disadvantage. One must know in advance what components will be present and the instrument modified to detect a specific chemical. The level of the chosen component must be representative of the level of total hydrocarbon emissions. The primary use of IR analysis may be as a detector in some other form of analysis system.

b. Combustion Analyzers — Two types of instruments of this type are available. In the first, the sample stream, mixed with air if necessary, is passed over a heated platinum wire which catalytically oxidizes the hydrocarbons. The heat of combustion causes the wire to heat up which changes its resistance. The wire forms one leg of a bridge circuit. The change of resistance unbalances the bridge and this is used as a measure of total combustibles.

The disadvantage of this system is that the platinum is easily poisoned and so cannot be depended upon to have constant activity over a period of time. Also, for simple hydrocarbons the heat of combustion follows a regular pattern with the number of carbon atoms. For more complex molecules, the heat of combustion follows a more variable pattern so that one must know the principle components present to relate instrument output to total hydrocarbons. Finally, other combustibles, such as CO, interfere with the analysis.

In another type of combustion analyzer, the organics are burned completely over a catalyst such as copper oxide. The CO_2 produced is measured, typically by infrared, and is used as a measure of total hydrocarbons. Poisoning is not a problem here and response depends only on the number of carbon atoms and not on the particular molecules present. The presence of CO_2 and CO in the original sample interferes with the analysis and must be determined separately. Dual column chromatographic techniques, with backflushing, have been used with this type of system, but are not applicable to continuous monitoring.

c. Flame Ionization Detection — This technique is probably the most promising at the present time. When hydrocarbons pass through a hydrogen flame they are ionized. This enables the flame to carry an electrical current. By measuring this current, it is possible to get a measure of the carbon atoms present. The method is not sensitive to CO_2, CO or water vapor. It adapts easily to continuous measurements and is the most sensitive to low concentrations. Furthermore, instruments are commercially available which are entirely enclosed in a temperature controlled oven which allows operation at high temperatures.

The chief disadvantage is that the principal components of the stack must be known. Response for simple hydrocarbons is regular with carbon number. However, correction factors must be applied if the stream contains significant amounts of hydrocarbons containing oxygen or other groups. In extreme cases, calibration mixtures will be required. Also, the instrument requires a supply of hydrogen and pure air or oxygen. A schematic of a typical flame ionization detector system set up for continuous measurement is shown in Figure 39. Particulate and aerosol must be excluded from the sample stream prior to the hydrogen flame.

d. Gas Chromatography — The previous methods attempt to measure total organics without regard to identification of individual components. (Infrared can be used for the latter purpose but it requires a far more elaborate and sophisticated instrument than is usually used in air pollution analysis.) Gas chromatography, on the other hand, permits a separation of a sample into its components. A detector, usually thermal conductivity or flame ionization, is then used to identify and measure the fractions. A wide variety of techniques and columns are available to permit identification of practically any material that may be encountered. The requirements can be quite elaborate, however, and do not lend themselves to field use. Nor is GC suitable for continuous monitoring. Also, the multiplicity of components usually involved may make column selection difficult. It is useful as a support device for the previously described devices.

C. E.P.A. Test Methods*

The location of the instrumentation relative to the sample source, necessitated transporting the sample more than 100 feet through a heated sample transport system (Figure 40), consisting

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*This section has been adapted from a report prepared for the E.P.A. by Scott Laboratories, Plumsteadville, Pa. The technique described herein was devised for sampling a particular plant and may not be completely general in its applicability.

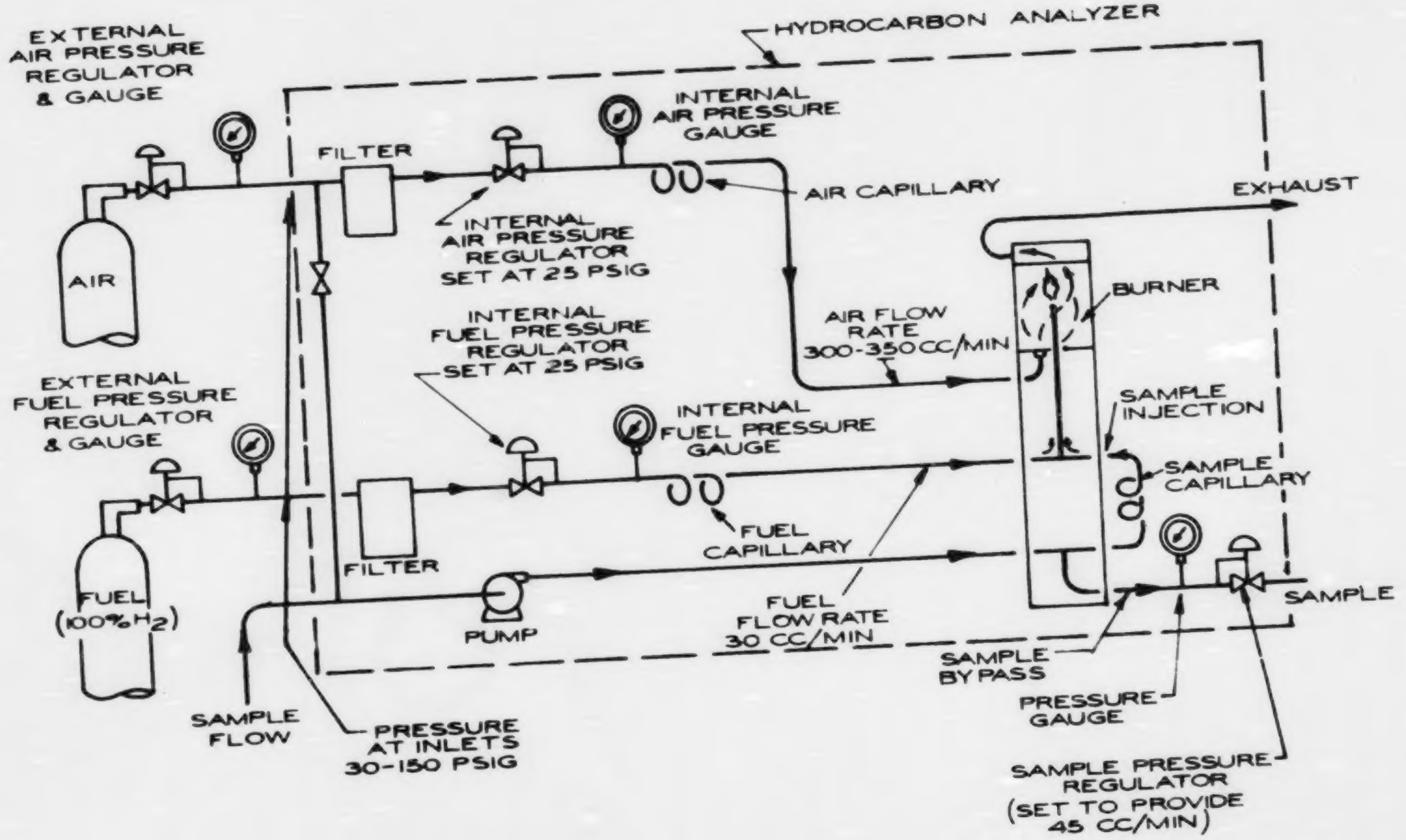
HYDROCARBON ANALYZER
EXTERNAL AIR PRESSURE REGULATOR & GAUGE
AIR
FILTER
INTERNAL AIR PRESSURE GAUGE
AIR CAPILLARY
EXHAUST
INTERNAL AIR PRESSURE REGULATOR SET AT 25 PSIG
BURNER
AIR FLOW RATE 300-350 CC/MIN
INTERNAL FUEL PRESSURE REGULATOR SET AT 25 PSIG
EXTERNAL FUEL PRESSURE REGULATOR & GAUGE
INTERNAL FUEL PRESSURE GAUGE
SAMPLE INJECTION
SAMPLE CAPILLARY
FUEL CAPILLARY
FILTER
FUEL (100% H2)
PUMP
FUEL FLOW RATE 30 CC/MIN
SAMPLE
SAMPLE BY PASS
SAMPLE FLOW
PRESSURE AT INLETS 30-150 PSIG
PRESSURE GAUGE
SAMPLE PRESSURE REGULATOR (SET TO PROVIDE 45 CC/MIN)

FIGURE 39

SCHEMATIC FLOW DIAGRAM OF FLAME IONIZATION DETECTOR

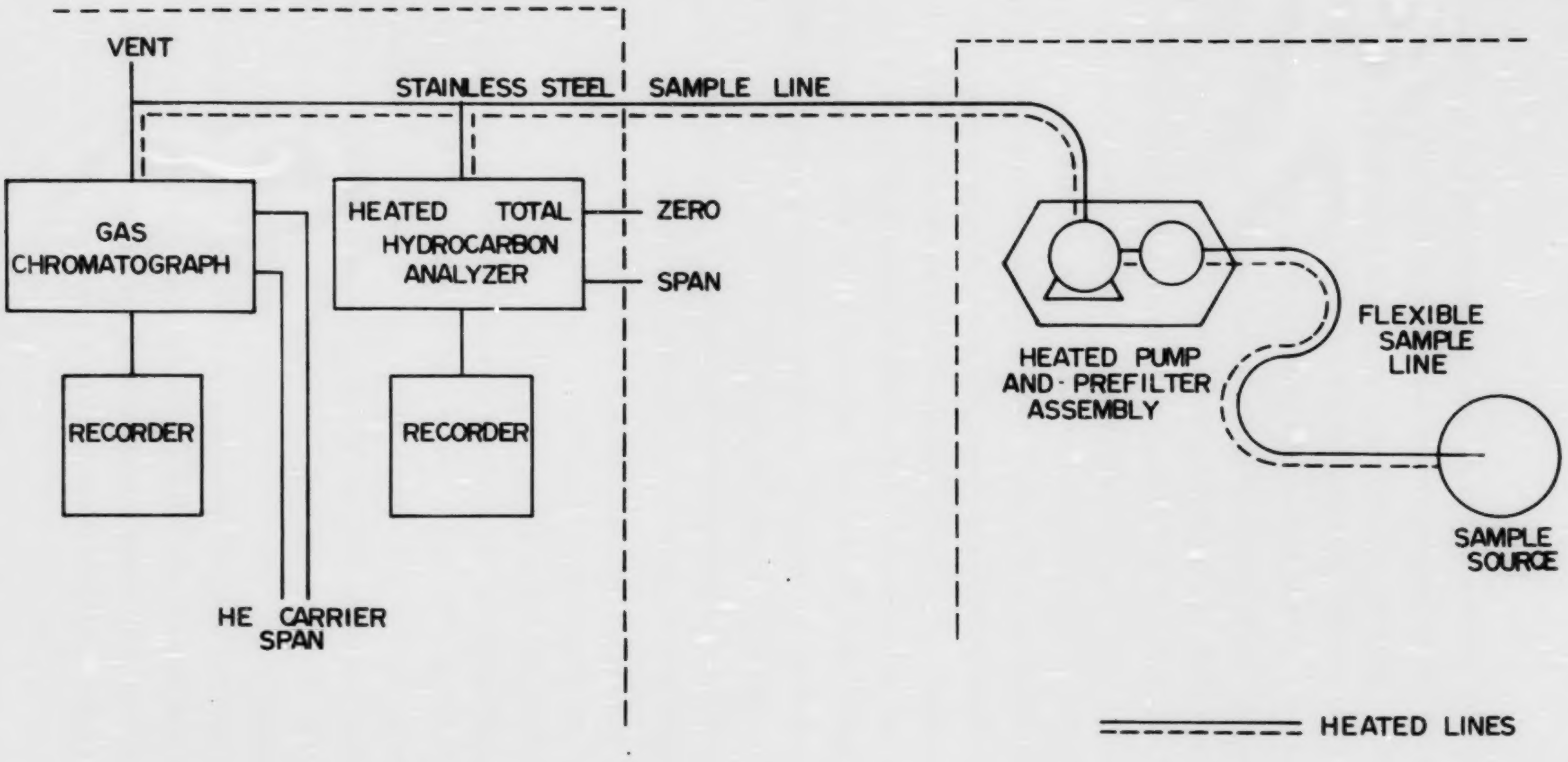

FIGURE 40
HYDROCARBON MONITORING SYSTEM

of a 1/4" O.D. x 18" stainless steel sample probe connected to six feet of externally heated 1/4" O.D. teflon sample line. This flexible section of sample line was connected to a heated 7 cm clamshell prefilter joined to a heated stainless steel bellows pump. From this point the sample was transported approximately 100 feet through resistance heated 3/8" O. D. stainless steel tubing. With the exception of the sample probe all components of this system were maintained at approximately 250°F to prevent hydrocarbon losses due to condensation. The hydrocarbon analyzer and gas chromatograph were connected in parallel at the end of this section of sample line.

Total hydrocarbons were continuously monitored with a Scott Model 215 heated total hydrocarbon analyzer, utilizing a flame ionization detector. The detector bench and sample pump were maintained at 300°F to prevent condensation losses of high molecular weight hydrocarbons. The analyzer was optimized to yield an oxygen response of less than 0.2%. The carbon response linearity was checked by comparing hexane, toluene and propylene standards against propane. The average carbon response for the three classes of hydrocarbons was 98.9%. The instrument was spanned with "Close Tolerance" (±2.0% analysis) blends of propane in air and zeroed with hydrocarbon free air (<0.1 ppm C_1). The fuel and oxidant for the flame ionization detector were 40% hydrogen in helium and blended air respectively. The continuous total hydrocarbon trace was recorded on a Texas Instrument Servo/Riter II recorder.

For all tests the sample backpressure was maintained at 2.0 psig with a bypass flowrate of 6 SCFH. The analyzer was zeroed and spanned before and after each test and at regular intervals during each test. In order to correlate total HC emissions with process conditions, notations were made on the charts of process mode changes, time checks, gas chromatograph injections, reactor temperatures and other pertinent information.

Each total hydrocarbon strip chart was divided into specific intervals based on the various modes of operation for each process cook. An average hydrocarbon level in ppm-C_1 was then calculated for each process interval. Mass emission rates in lb/hr were then calculated based on the average flowrates measured for each process interval. The mass emissions per tons of resin produced was calculated by first finding tons of resin produced per hour and comparing that with the mass emissions rate (lbs/hr).

While the T.H.C. analyzer was continuously monitoring hydrocarbon concentrations, point samples were injected periodically into a gas chromatograph. The gas chromatograph, a Varian Model 1200 equipped with a flame ionization detector and a (1 mv.) Texas Instrument Recorder was used to provide a qualitative and semi-quantitative analysis of the effluents from their kettles.

Ideally, for a quantitative analysis, it would be necessary to prepare a standard to analyze each component of the effluent. Since this was impractical, an alternate procedure, to give a semi-quantitative analysis, was chosen. Through proper manipulation of the fuel to oxidant ratio, the flame ionization detector of the gas chromatograph was rendered linear for carbon response. Linearity was checked by comparing cylinders of known concentrations of m-xylene, benzene, and n-hexane. The variation in response factor for these compounds was approximately 6%. Thus, a cylinder containing known carbon concentration (59.7 ppm m-xylene or 477.6 ppm C_1) could be used to determine carbon concentration of each component in the sample. Operating parameters for the gas chromatograph with the flame ionization detector are summarized below:

GAS CHROMATOGRAPH PARAMETERS

VARIAN MODEL 1200 GAS CHROMATOGRAPH

Parameters	Alkyd Solvent Cook	Polyester Cook	Alkyd Fusion Cook (soya)	Thinning
Detector Temp.	200°C	250°C	200°C	200°C
Gaseous Injection Sample Loop	.25 cm^3	1 cm^3	1 cm^3	1 cm^3
Column	IGEPAL Capillary (50' x .02" I. D.)	Poropak Q (3½')	IGEPAL	IGEPAL
Temp. Program	40°C-110°C @ 4°/min.	100°C-230°C @ 6°/min.	40°C-130°C @ 4°/min.	40°C-130°C @ 4°/min.
Fuel (H_2)				
Press (psi)	20	20	20	20
Flow Rate (cc/min.)	62.5	62.5	62.5	62.5
Oxidant (0_2)				
Press (psi)	35	35	35	35
Flow Rate (cc/min.)	600	600	600	600
Carrier gas (He) Flow Rate (cc/min.)	6	50	6	6

Expecting to see solvent emissions from the kettles, an IGEPAL (Nonyl Phenoxypoloxyethylene Ethanol) capillary column, (50' x .02" I. D.) was chosen to perform the analysis. With a quick qualitative analysis in mind, sample chromatograms were prepared from the vapors of various paints.

Then, having a previous knowledge of the paint solvents and holding chromatographic conditions constant, each component was identified by comparing its retention time to that of standards. Duplicating these chromatographic conditions in the field would enable a reasonable analysis to be performed.

After the initial testing of the stacks began, however, it became obvious that light solvents were involved in only the alkyd solvent cook, where xylene and ethyl benzene vapors were the major components of the effluent. The IGEPAL column, as field chromatographic conditions were designed, was not capable of handling the heavier constituents (high boilers) or the aliphatic hydrocarbons in the effluent of the alkyd fusion or polyester resin cooks. It was necessary therefore to obtain additional chromatographic data by taking five liter Tedlar® bag samples during the fusion and polyester cooks. These bags were returned to a laboratory where other columns and operating conditions could be utilized in an effort to identify and quantify the major hydrocarbons. Bag samples were also taken of the thinning tank emissions.

Several techniques were employed in an effort to obtain accurate stack gas flow rates at the various sampling locations. Most of the measurements were made with an S-type pitot tube and hook gauge capable of measuring pressure differentials of 0.002 to 2.000 inches of water. Where pressure differentials greater than 2.0 inches of water were found, a 10-inch water manometer was used. When the pitot tube was calibrated in the laboratory, a pitot factor of 0.850 was calculated for pressure readings of 0.01 inches of H_2O or greater. For pressure readings of less than 0.010, a pitot factor of 0.758 was calculated. For lower flow conditions where the pitot tube could not be used, two different bag samples were configured. The first of these consisted of a 5 cubic foot Tedlar® bag fitted with a tapered silicone rubber boot, large enough to fit over a three inch diameter stack. The flow measurement was made by attaching the bag to the desired stack opening and recording the time required to collect a sufficient volume of sample. The bag was then attached to a pump and evacuated through a dry gas meter to measure the volume collected.

This method proved to be adequate until it was noticed that some of the stacks were "breathing" i.e., drawing in ambient air and exhausting stack gases in a cyclic manner. This meant that a new system had to be configured that would permit only the measurement of the positive portion of the flow and not yield a net flow over the breathing cycle. This was accomplished by adding a silicone rubber one way flapper valve at the exit of the stack. Since the flow rate under these conditions was extremely low, a smaller 2.5 cubic foot bag was used. The inlet to the bag was fitted with the same silicone rubber boot used on the original bag, and the outlet connections used for evacuating the bag consisted of a short piece of 1/4" O.D. Teflon® tubing fitted with a syringe cap to prevent leaks during the sampling period. The bag was placed inside a cardboard box to protect it from the wind while sampling.

Flow measurements were made at half hour intervals during each process, when possible, and at more frequent intervals when process changes required. Stack gas temperatures were also measured in conjunction with each flow measurement.

II. CONTINUOUS SOURCE MONITORING TECHNIQUES USED BY INDUSTRY

Industry has generally not used continuous monitoring techniques on any kind of a routine basis. Sampling has been done on a "grab" or semicontinuous basis and then only as needed for a specific situation, such as design information or to gather emission data for operating permits. The grab samples have not proven to be too reliable and have further decreased the desire of industry to monitor emissions in any fashion.

A continuous hydrocarbon analyzer has been used by one manufacturer for monitoring emissions from resin manufacturing. The system uses an explosion proof flame ionization detector. The sampling line is fitted with an entrainment separator. This was supplemented with a gas chromatograph for determining the composition of the sample stream. Sampling was done at the condenser vents of the reactors. Their procedure did not include methods for determining particulate or aerosol loadings.

Some thermal and catalytic incinerator manufacturers also use continuous flame ionization monitoring of a kettle cook for determining design parameters. They usually measure only for the two or three cooks that represent the plant's maximum emissions.

The continuous monitoring of emissions from an incinerator outlet could be very successfully applied. All problems of condensation, line plugging and hold up of heavy materials in the sample train should be eliminated after the gases have been incinerated.

How well the flame ionization detector would stand up under continuous use is not known; however, it is anticipated it would require more service and operator time than the incinerator itself.

This flame ionization detector could also be used for control of hydrocarbon concentration at an incinerator outlet. This would be especially helpful and adaptable for catalytic incineration. Control would be accomplished by adjustment of the catalyst temperature to compensate for decrease in catalyst activity as the catalyst ages with time.

CHAPTER 4

INVENTORY OF EMISSIONS

I. EMISSION FACTORS FOR EACH SOURCE

The emission data reported in the questionnaires has been examined in an effort to correlate quantity of emission with production volume. A primary reason for this effort was to obtain an approximate geographical distribution of air pollution "potential" for the industry. Those sections of the questionnaires dealing with emissions were on the whole the least comprehensively filled out. Fewer than 10% of the questionnaires reported sufficient information to enable an estimated emission factor to be computed. The extreme variations in the calculated values and the lack of any discernable pattern casts some doubt on the realiability of the estimates so obtained.

Three types of emission factors were sought. From plants which make coatings only (no resins or varnish), pounds of gaseous emissions per million gallons *solvent based* coatings and pounds of particulate emission per million gallons of all types of coatings were correlated. These distinctions were made on the assumption that most gaseous emissions are attributable to solvent based coating production and that particulate emission, mainly pigment, are attributable to most surface coating production. Table 47 presents the emission factors calculated from these plants.

Plants which manufacture only resins were used to obtain pounds of gaseous emissions per million pounds of resin solids. This data is summarized in Table 48.

Plants which produce both finished coatings and resins permitted the calculation of all three types of emission factors. Data from plants in this category were used only where particular emissions reported could be assigned to either paint or resin production with some degree of confidence. Information from these plants is summarized in Table 49.

Only those plants whose emission inventory was reasonably inclusive of most of the major sources were used. Major sources in this context include raw material handling and storage operations, reactor vents, filling operations, ventilation hood exhaust vents, and general building exhaust systems. Most emission data was reported in pounds per hour. This was multiplied by the number

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TABLE 47

EMISSION FACTORS FROM SELECTED PAINT PLANTS

Plant	Gaseous (lb/MM gal solvent based)	Particulate (lb/MM gal)
2A	8,800	
2B	21,000	
2C	71,500	
2D	45,800	
2E	102,800	
2F	89,300	
2G	7,700	
2H	141,200	
2I	—	295,000
2J	95,900	
2K	9,200	
2L	104,000	
2M	15,900	
2N	—	58,100
2O	—	3,600
2P	25,200	
2Q	46,100	
Average	56,000	—

Source: Questionnaire data

TABLE 48

EMISSION FACTORS FROM SELECTED RESIN PLANTS

Plant	Gaseous (lb/MM lb resin solids)	Principal resin types
3A	87,600	Polyester, alkyd
3B	2,600	Alkyd, varnish
3C	1,750	Rosin types
3D	1,700	Water based acrylic
3E	21,100	Water based vinyl
3F	162	Acrylic (water & solvents)
3G	15,350	Hydrocarbon
3H	1,120	Alkyd, water based vinyl
3I	12,600	Varnish
3J	10,500	Amino, polyester
3K	3,400	Epoxy
3L	19,500	Epoxy
3M	1,300	Alkyd, polyester
3N	73,150*	Vinyl (solvent and water)
Average	13,700	

*Most of this emission is from "resin dryer" operation.

Not included in average.

Source: Questionnaire data

TABLE 49

EMISSION FACTORS FROM SELECTED PLANTS PRODUCING COATINGS AND RESINS

	Resin Production	Coating Production	
Plant	Gaseous (lb/MM lb)	Gaseous (lb/MM gal solvent based)	Particulate (lb/MM gal)
1A	— —	36,800	
1B	824	5,300	19,400
1C	560	22,000*	
1D	— —	113,000	
1E	1,100	46,400	
1F	1,800	35,100	
1G	22,000	37,700	
1H	6,500	65,000	
Average	5,460	45,000	— —

*In addition to this, the plant also emits 235,000 pounds/year from spray booths and drying ovens.

Source: Questionnaire data

of plant operating hours per year on the assumption that the source in question operates at the stated emission rate for the same number of hours. In some cases, at least, this assumption is probably not correct. Emissions were correlated for the uncontrolled process assuming no emission control devices.

No particular pattern has emerged to help interpret the results summarized in Tables 47 to 49. The magnitudes of the emission factors calculated for coating production, for instance, show no dependence on solvents used, production volume, per cent industrial sales, etc. Similarly, emissions from resin production do not seem to correlate with types of cooks, types of resins, or solvents used. In any event, simple averages were calculated and are also presented in the Tables. No attempt was made to average the particulate emissions due to wide scatter and few data points.

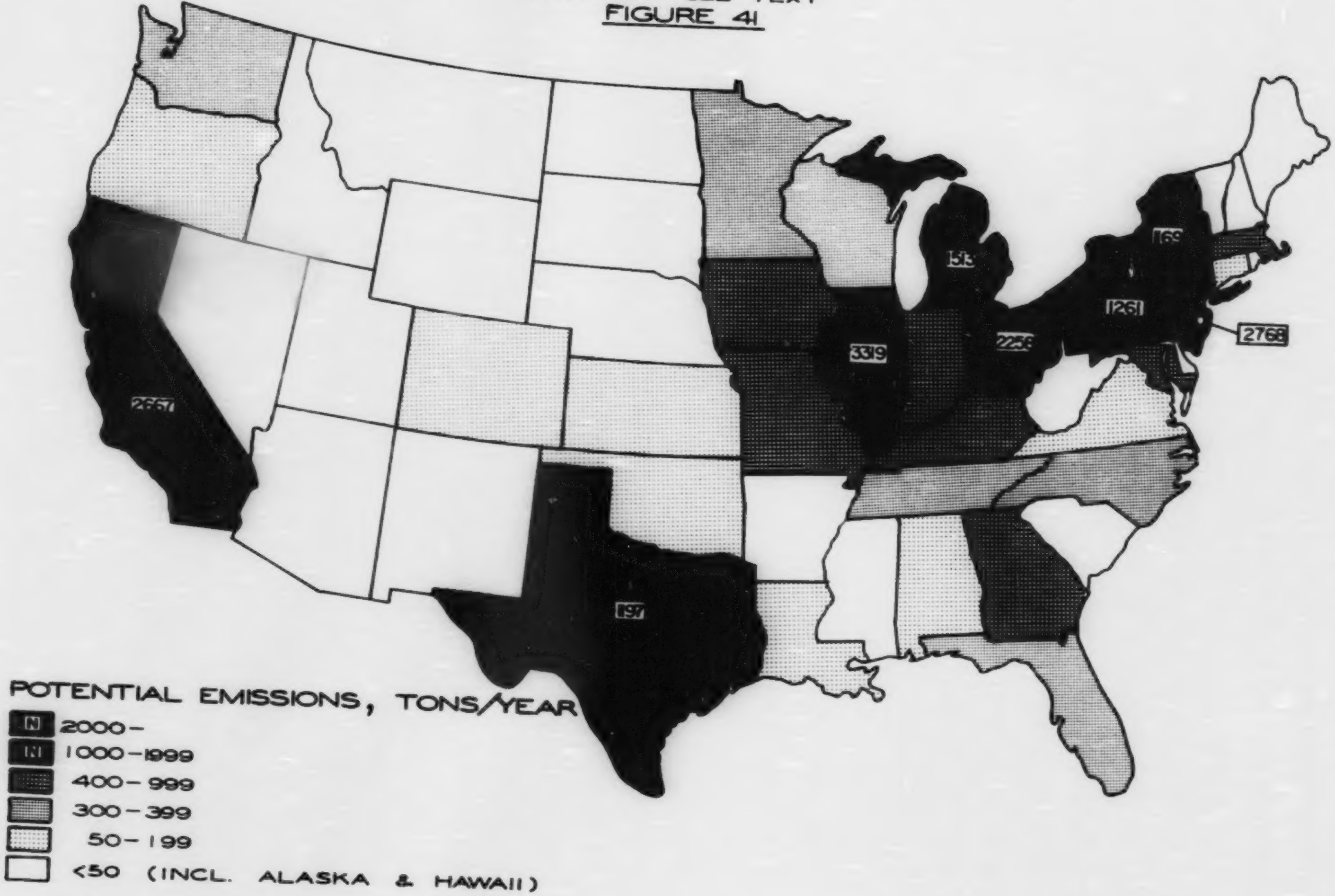
II. EMISSION INVENTORY FOR THE INDUSTRY

The emission factors obtained above permit one to estimate potential emissions for a geographical area for which production figures are available. Production by states has been estimated for 1972 in Chapter 2. Using these outputs and assuming a uniform ratio of solvent based production (77% of total gallons produced), gaseous pollution potential from uncontrolled paint manufacturing operations has been estimated for each state. The results are presented in Figure 41. An average emission factor of 50,000 pounds gaseous emissions per million gallons of solvent based paint was used in the calculation. Total gaseous emissions for the U.S.A. from paint production are estimated to be 23,200 tons for the year 1972.

The emission factors presented in this section can be applied to the model plant discussed in Chapter 1. The model plant produces 1.1 million gallons of solvent based paint and 2.1 million pounds of resin solids. Based on the average emission factor for this type of plant given in Table 49, the model plant should emit $(1.1 \times 45{,}000) + (2.1 \times 5{,}460) = 60{,}966$ pounds per year of gaseous emissions. The source-by-source calculation in Chapter 1 totaled 65,590 pounds. The two calculation methods agree quite well as far as totals are concerned. The relative amounts of emissions attributable to resin production as opposed to paint production show wider variations between the two methods. The emission factors predict less from paint production and more from resin production.

The degree of consistency between the two methods is remarkable considering the extreme scatter present in the emission factor data and the assumptions used in the model plant calculation. It would be unwise, however, to draw any strong conclusions concerning the applicability of either approach to coatings manufacturing operations selected at random.

GEOGRAPHICAL DISTRIBUTION OF
ORGANIC EMISSIONS
FROM PAINT PRODUCTION 1972
SOURCE: SEE TEXT
FIGURE 41



CHAPTER 5

EMISSION CONTROL TECHNOLOGY

In this chapter a detailed discussion of the existing state of the art of air pollution control for this industry will be presented. The discussion will include a description of the best control technique for each emission source, alternate control techniques, methods of control other than add on equipment, types of performance of currently used systems and capability of best control systems to meet more stringent standards. Potential water and solid waste disposal systems will also be reviewed.

I. DESCRIPTION OF BEST CONTROL SYSTEMS

As discussed in Chapter 1, the two main types of non-fugitive emissions are gaseous organic pollutants and pigment and resin particulate. The best control techniques for these pollutants are discussed below.

A. Control of Particulate Emissions

The best control device for pigment and resin particulate is a fabric collector. The system for collecting and controlling pigment dust during the loading operation of mixers, ball mills and the like is shown in Figure 42. Depending on the plant layout there may be one or more of these systems. The principal part of the system is the baghouse or fabric filter. It is by far the best control device and is ideally suited for this application. Collection efficiency of the submicron pigment particulate (0.05 to 0.25μ) is very high, in the range of 99.9%. The gas stream is low temperature and the grain loading is low. The collected product can be recycled for use in dark primer paints. The installed cost for this system can be quite expensive, depending upon the collection system used. Basically there are two types. A fixed collection hood for each loading station that collects both dust and empty pigment bags or a movable flexible hose that can be placed at one or more loading stations while the pigment bags are being emptied. In some cases the hose is connected directly to the mixing tank and ventilation air is drawn through the loading hatch with the pigment particulate. This is a very efficient method of capturing the fugitive dust. The disadvantage occurs due to increased solvent losses from the mixing tank.

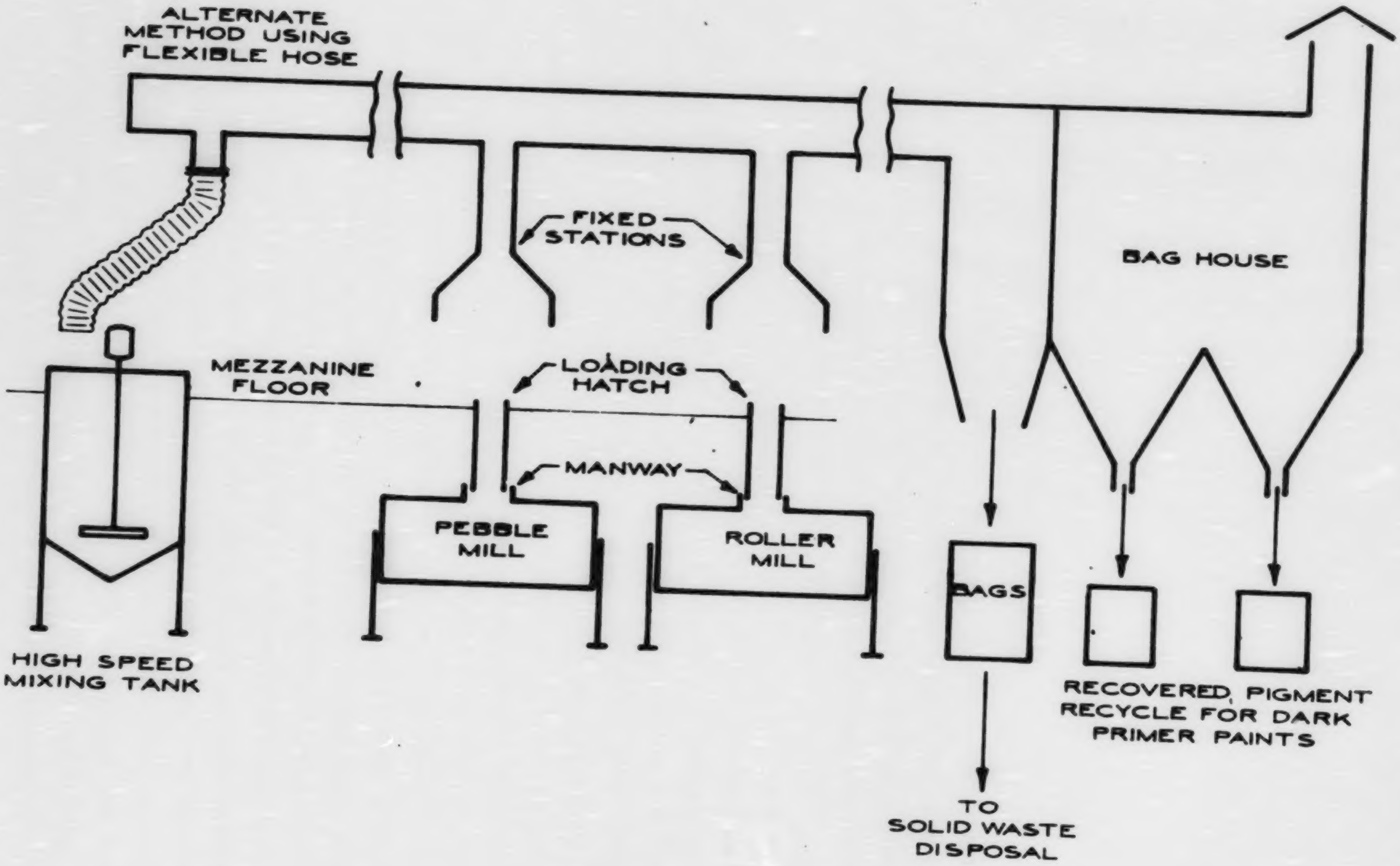


FIGURE 42
PIGMENT EMISSION CONTROL SYSTEM

There is a large variety of baghouses currently available as "off the shelf" items from over a dozen manufacturers. They all operate in essentially the same manner. The pigment laden air is filtered by the cloth tube or bags contained in the house. The house itself is divided into four sections — the dirty air plenum, the bag area, the clean air plenum and the particulate collection hoppers. The function of the two plenums is to properly distribute the air flow to and from the bags. Many types of bag materials may be used, but woven cotton bags are not only adequate but also the least expensive and, therefore, the most commonly used for this service. The collected particulate needs to be periodically cleaned from the bags. This can be done either intermittently or continuously. Intermittent baghouses are designed for periodic cleaning, such as once a day, and are easily adapted to the low dust loadings and batch operation encountered in the paint industry. They are normally the lowest cost baghouse. Continuous baghouses are cleaned automatically and are able to operate 24 hours per day. They can also handle high dust loadings.

Cleaning of the bags can be accomplished by a variety of methods which includes shaking the bags, reversing the air flow through the bags, blowing a jet of air on the bags from a reciprocating manifold, or rapidly expanding the bags by a pulse of compressed air. The method most commonly used with the intermittent baghouse is shaking which can be done manually at the end of a days operation. The bags in a shaker-type baghouse are supported by a structural framework which is free to oscillate. If this type of baghouse is used on a continuous basis the bags are cleaned automatically. Periodically, by use of a timer, a damper isolates a compartment of the shaker baghouse so that no air flows. The bags in the isolated compartment are then shaken for a minute or so, during which time, the collected pigment or resin is dislodged and falls into the baghouse hoppers. Another type of continuous baghouse commonly used in this industry, as characterized by its cleaning method, is the reverse pulse baghouse. This type utilizes a short (100 millisecond or less) pulse of compressed air through a venturi or diffuser. The primary air pulse is directed from the top to the bottom of the bag and aspirates secondary air as it passes through the venturi. The resulting high flow air pulse travels the length of the bag rapidly expanding the cloth and dislodging the collected dust cake.

The primary variable used in applying a baghouse to this or any application is the air-to-cloth ratio as defined below:

$$R = Q/A$$

where: R = air-to-cloth ratio, feet/min

Q = volumetric air flow, ACFM

A = net cloth area, ft^2

Air-to-cloth ratios normally run from 1 to 3 for shaker and reverse air baghouses while reverse pulse units will run between 5 and 18. The basis for selection will vary with dust loading, dust type, desired bag life and allowable pressure drop. Typical air-to-cloth ratio utilized in the paint industry are 8.4/1 for a reverse pulse jet baghouse with polyester bags and 2/1 for a shaker baghouse with cotton satin bags.

In most cases, pigment emissions are of a minor nature and do not violate existing air pollution control regulations. Because of this and the extra cost involved, the use of a baghouse collection system is not a wide spread practice. Those in existence have been motivated by occupational health, good housekeeping and product recovery.

A similar problem exists for resin manufacturing plants in the grinding or flaking of the hardened resin. The same approach is normally used. The air from the baghouse may still contain a significant odor and further treatment may be required if a local nuisance exists.

B. Control of Gaseous Emissions

The best control technique for gaseous emission from the paint and varnish industry is oxidation or combustion of the organic pollutants to CO_2 and H_2O. This is the only control technique currently being used that has proven effective for all cases. Three general methods are employed to oxidize waste gases, as follows:

Flame Incineration or Direct Combustion
Thermal Combustion or Oxidation
Catalytic Combustion or Oxidation

All of the above methods are oxidation processes. Ordinarily, each requires that the gaseous effluents be heated to the point where oxidation of the combustible will take place. The three methods differ basically in the temperature to which the gas stream must be heated. These methods will be briefly described for better understanding of their application to the paint and varnish industry.

1. Flame Incineration

Flame incineration is the easiest of the three to understand, as it comes the closest to every day experience. When a gas stream is contaminated with combustibles at a concentration approaching the lower flammable limit, it is frequently practical to add a small amount of natural gas as an auxiliary fuel and sufficient air for combustion when necessary, and then pass the resulting mixture through a burner. The contaminants in the mixture serve as a part of the fuel. Flame incinerators of this type are most often used for closed chemical reactors. Figure 43 is a schematic illustration of a flame incineration unit. This unit resembles a flare operated within a combustion chamber

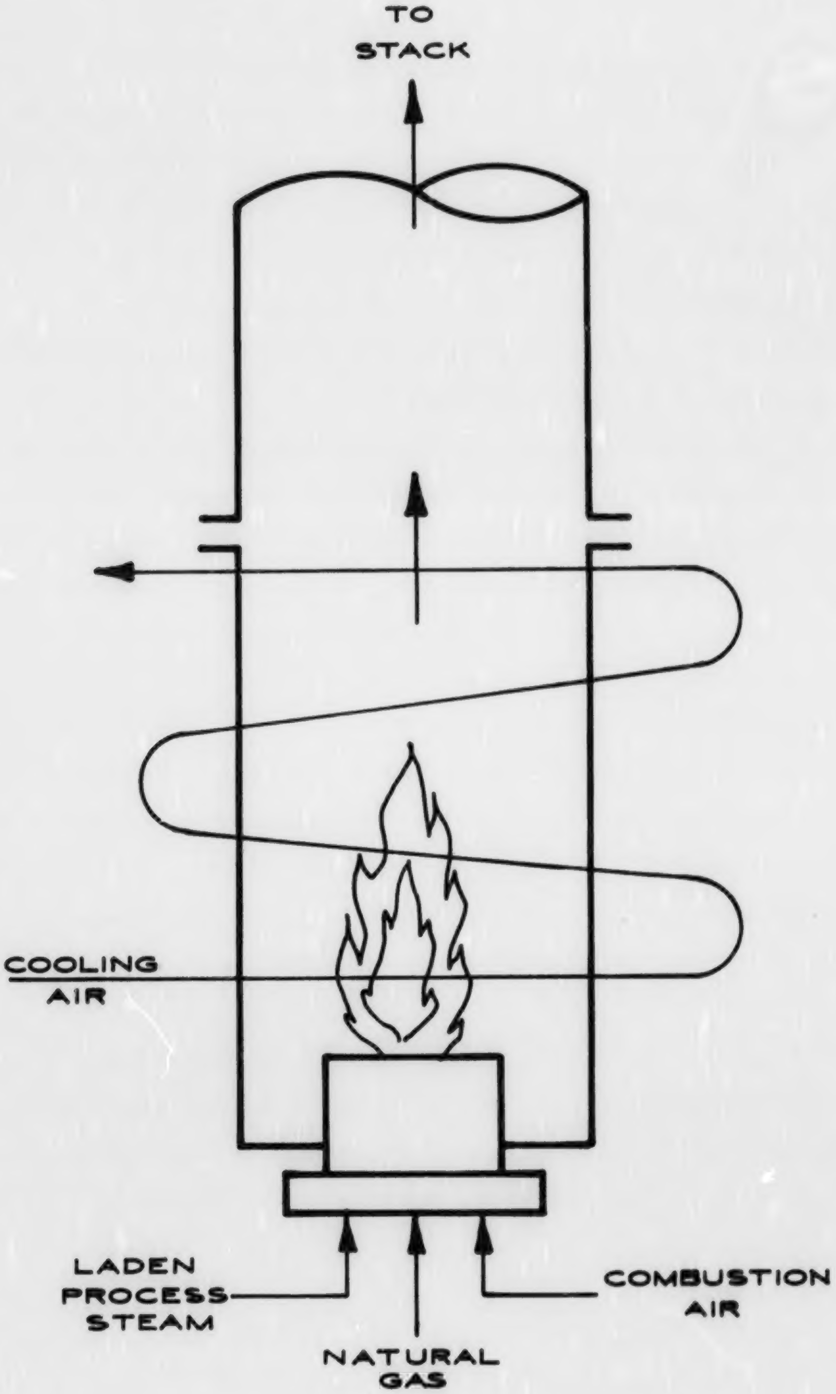


FIGURE 43

SCHEMATIC DIAGRAM OF A FLAME INCINERATION UNIT where the combustion conditions may be controlled carefully.

Flame incineration cannot be used for open kettle cooking because of the high volume and low combustible concentration of the exhaust. It would be ideally suited for closed reactor kettles if these could be run at a high enough pressure to supply the driving force through the system. Unfortunately most kettles must be opened periodically for additions of various materials such as pentaerythritol and phthalic anhydride. Also, many resin cooks must be run under a vacuum. Aside from these limitations, a suitable transfer line would have to be developed to be both functional and comply with insurance safety requirements.

Flame incineration systems are generally difficult to handle with regard to either self-recuperative or makeup types of heat exchangers because of the extremely high temperature of the effluent from the combustion chamber. For this reason, it is usually most economical to provide a steam generator to recover the waste heat rather than a gas-to-gas heat exchanger. With water as the cooling fluid, the hot side of the heat exchanger may be exposed to the temperatures generated in the combustion zone.

2. Thermal Combustion

It is far more likely that the concentration of combustible contaminants in an air stream will be well below the lower limit of flammability. When this is the case, thermal oxidation is considerably more economical than flame incineration. Thermal oxidation is carried out by equipment such as that illustrated schematically in Figure 44. In this equipment, a gas burner is used to raise the temperature of the flowing stream sufficiently to cause a slow thermal reaction to occur in a residence chamber.

Whereas flame temperatures bring about oxidation by free radical mechanisms at temperatures of 2500°F,[27 28 29] high conversions are produced by thermal afterburners at temperatures in the order of 1400°F with 1/2 second residence time.[27 28 29] Thermal afterburners can operate at conversion efficiencies in excess of 97% depending upon a number of operating variables. These conditions can be summarized as follows:

a. Operating Temperature
b. Quantity of Hydrocarbon
c. Residence Chamber Size or Residence Time
d. Type of Fume
e. Uniformity of Temperature — Good Mixing

The theoretical aspects of the reaction kinetic for thermal oxidation are discussed on the following page.

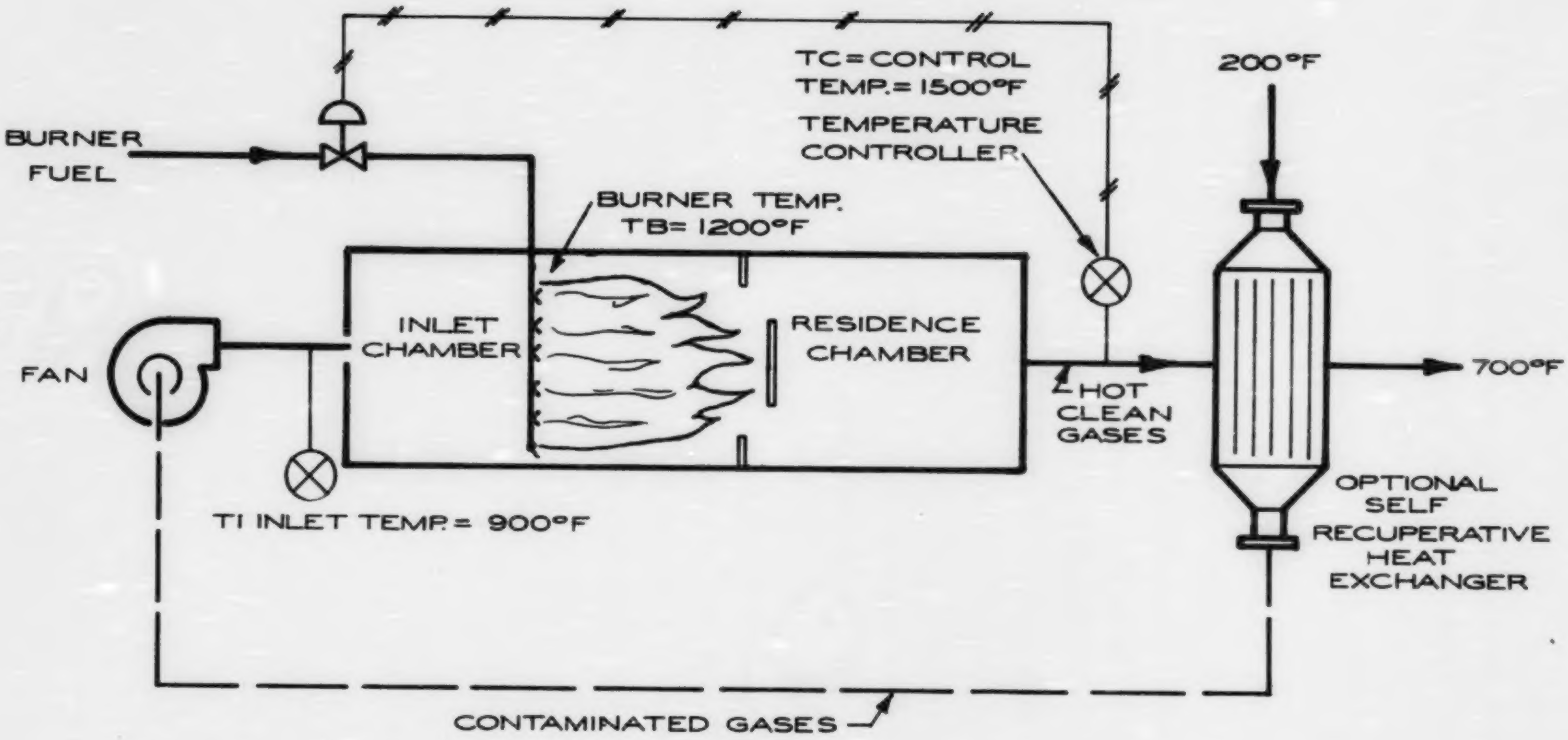


FIGURE 44

SCHEMATIC OF TYPICAL THERMAL AFTERBURNER AND CONTROL SYSTEM

If a gas containing species A and B which react to produce C, such that there is substantially no reverse reaction of C decomposing into A and B, we can write the equation

$$A + B \rightarrow C$$

or for the reaction of a hydrocarbon in air

$$Hc + O_2 \rightarrow CO_2 + H_2O$$

For flow processes, let us assume steady state conditions of a gas stream passing through a tube with good uniformity across any given cross-section. The concentration of Hc, O_2, CO_2, and H_2O will vary with time as an element of the flowing fluid moves through the reactor, or with distance, in that time and distance into the reactor are interchangeable for steady-state conditions.

We can expect the concentration of Hc and O_2 to drop off and can define the rate of disappearance of Hc as follows:

$$R = -k\,(Hc)^m\,(O_2)^n$$

where:

R = Rate of disappearance of Hc, mol/hr

k = Reaction Rate Constant, function of temperature

(Hc) = Concentration of Hc, mol/fraction

(O_2) = Concentration of O_2, mol/fraction

For almost all cases, including varnish cooking, the O_2 content of the gas stream is high and the Hc content is low. Because of this, the O_2 concentration is substantially constant and can be omitted. The exponent of (Hc) can be taken as 1.

$$R = -k\,(Hc)$$

Using x as the concentration of combustible:

$$\frac{dx}{dt} = -kx \text{ or } \frac{dx}{x} = -kt$$

Integrating this gives $x = Ae^{-kt}$

Using initial conditions $x = x_0$ at $t = o$

$$x = x \text{ at } t = t_1$$

$$x_0 = Ae^0 \text{ or } A = x_0$$

$$\frac{x}{x_0} = e^{-kt}$$

If conversion is defined as: $c = \dfrac{x_0 - x}{x_0}$

Then $1 - c = e^{-kt}$

From this, knowing the reaction rate constant and residence time, the conversion can be easily predicted. This formula applies directly only for an isothermal system. However, for most afterburner applications of contaminated air, k is a function of temperature which varies along the length of the afterburner. Calculation of conversion, then, requires a more lengthy solution of the rate equation over differential elements of the incinerator.

Past research indicates that most combustibles follow the pseudo first order reaction pattern described above and rate constants can be correlated by plotting ln k vs. $\frac{1}{T}$.

The few points required to plot these curves are experimentally determined in the laboratory by measuring conversion rates for a known combustible material at two or more operating temperatures in a reactor of fixed residence time.

This type of experimental work, to our knowledge, has not been done on open or closed varnish or resin kettle fumes. Experimental work on other hydrocarbon vapors indicates, however, that general guidelines can be applied to this type of contaminant. For example, 0.3 to 0.6 seconds residence appears to be the optimum range of reaction time and has been adopted as a standard by most afterburner manufacturers and air pollution regulatory bodies.

Figure 45 shows a relationship between temperature and residence time at a fixed conversion level of 95% and fume concentration of 2 Btu/SCF.

Figure 46 shows the relationship between conversion and temperature at a fixed residence time of 0.6 seconds.

Most afterburners are capable of operating at a temperature high enough to oxidize any organic material, except carbon particulate, and the actual operating temperature can be developed for a given type of afterburner after installation by trial and error. It is important when this approach is taken to insure the afterburner has at least 0.6 seconds residence time and the ability to operate at 1500°F.

Afterburners are designed to operate at a controlled outlet temperature and heat is added by the burner to the contaminated air stream to be incinerated until this temperature is obtained. Assuming the burner outlet is set high enough for the oxidation reaction to initiate, the heat of reaction of the combustibles will also be added to the air stream in the afterburner. This, in turn, will reduce the heat requirements of the burner. Less fuel will be added to the burner. Temperature rise across the afterburner will increase and the afterburner inlet temperature will drop. The gas temperature in the residence chamber now varies from inlet to outlet. The higher the fume loading the greater the temperature variation across the afterburner. If the afterburner outlet temperature is

FIGURE 45

RESIDENCE TIME VS. TEMPERATURE
AT
95% CONVERSION & 2BTU/SCF

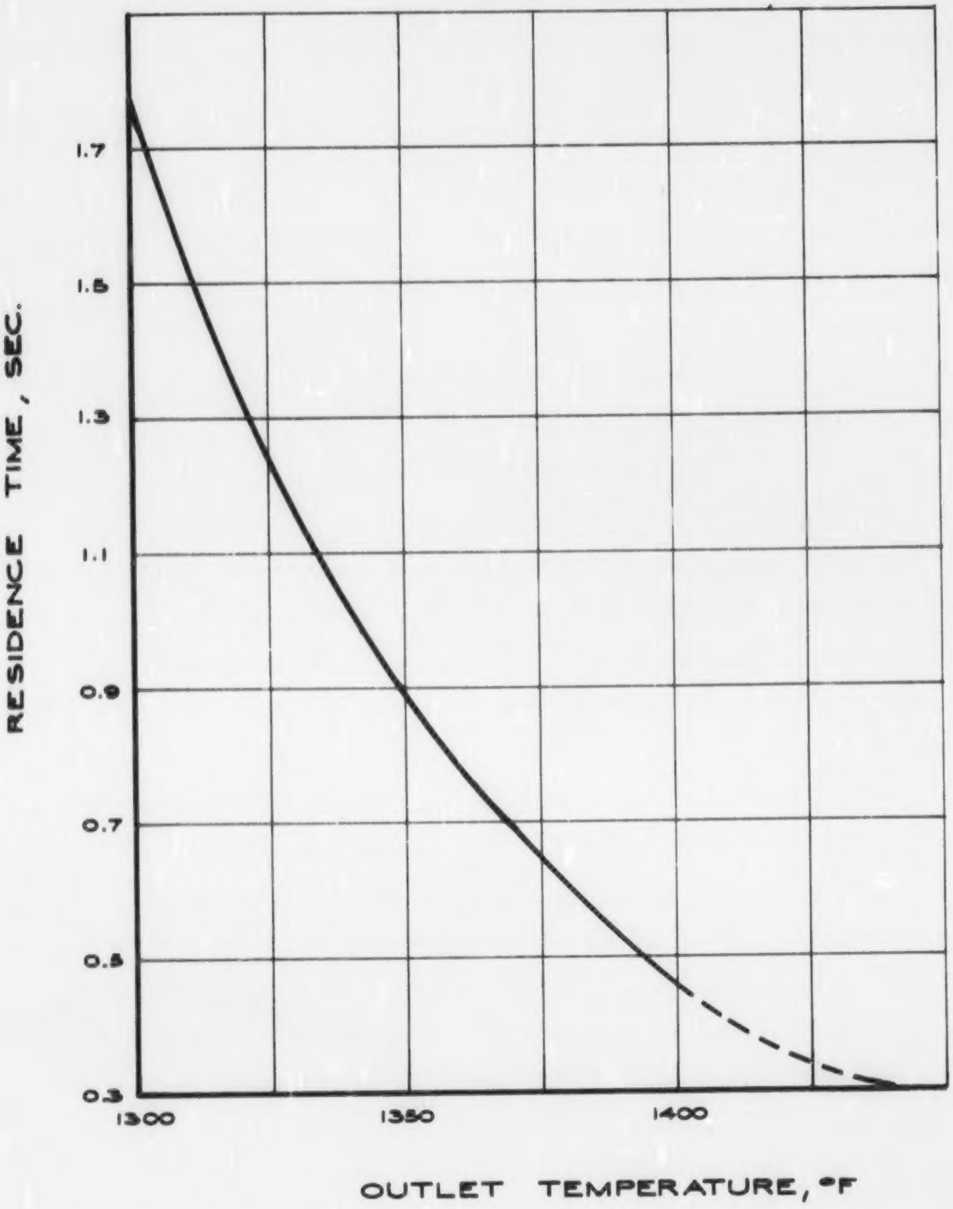
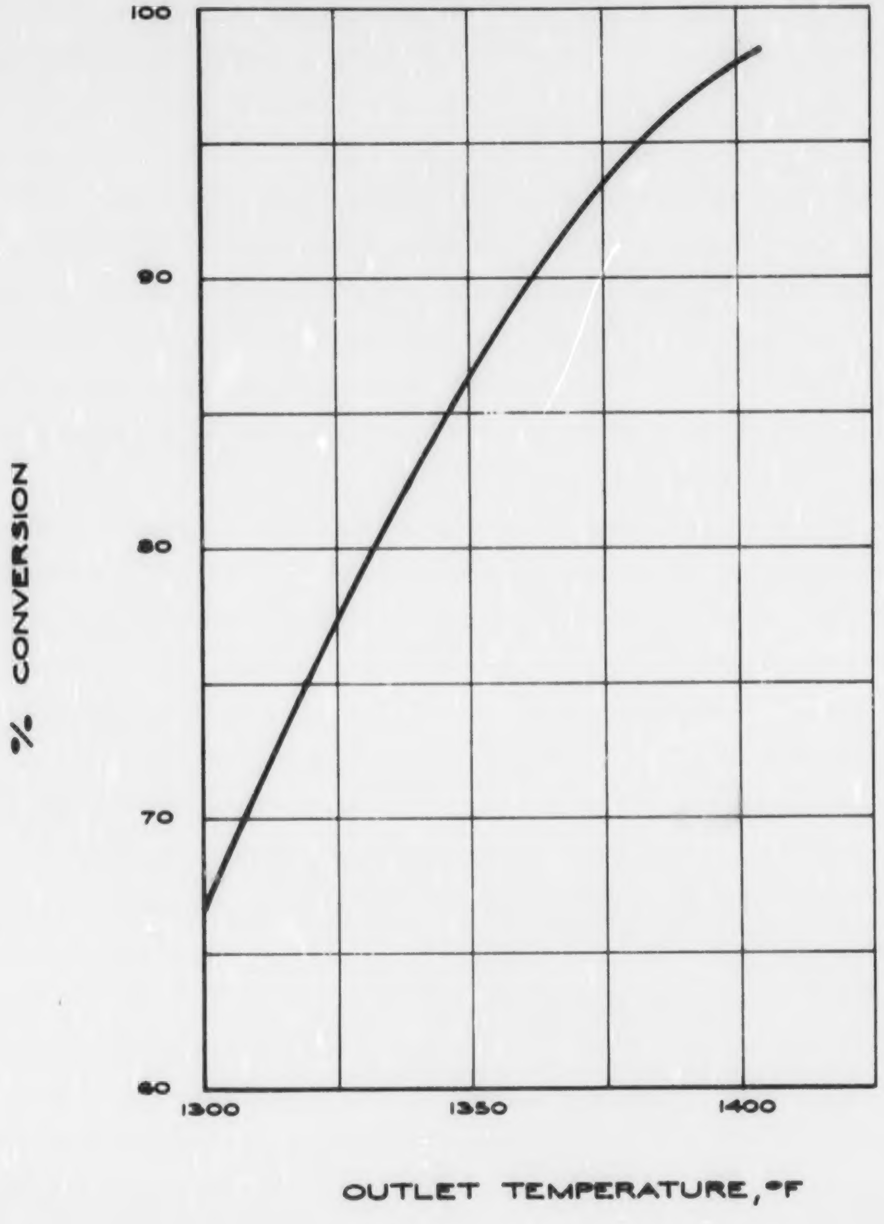


FIGURE 46

CONVERSION VS. TEMPERATURE
AT
0.6 SEC. RESIDENCE TIME & 2BTU/SCF



held constant, the average temperature in the afterburner will decrease as the fume load increases. Since the reaction rate is a function of temperature, it will also decrease.

The theoretical relationship between conversion and fume loading at a fixed outlet temperature and residence time is described in Figure 47. This relationship is applicable only to systems having a fixed outlet temperature. If the inlet temperature is held constant, the opposite effect will occur and conversion efficiency could increase with higher inlet concentrations. This is due to the first order dependence of oxidation rate on initial concentration, the effect of local heat of reaction, the effect of increased concentration of free radicals and the higher reaction temperatures reached. These effects are discussed in more detail in the *Afterburner Systems Study*, EPA Contract EHS-D-71-3.[27]

From the above discussion, it can be seen that for a given conversion level, the higher the fume load the higher the outlet temperature must run to assure the required conversion. In fact, for very high fume loads, if the outlet temperature is not set high enough, the temperature out of the burner can drop below the reaction initiation temperature and the reaction will cycle on and off.

Field experience indicates the above discussion is not applicable at low fume concentrations. This is caused by difficulties of measurement, generation of combustible material from the burner, and generation of small quantities of partially reacted material that are normally insiginificant at high fume concentration levels.

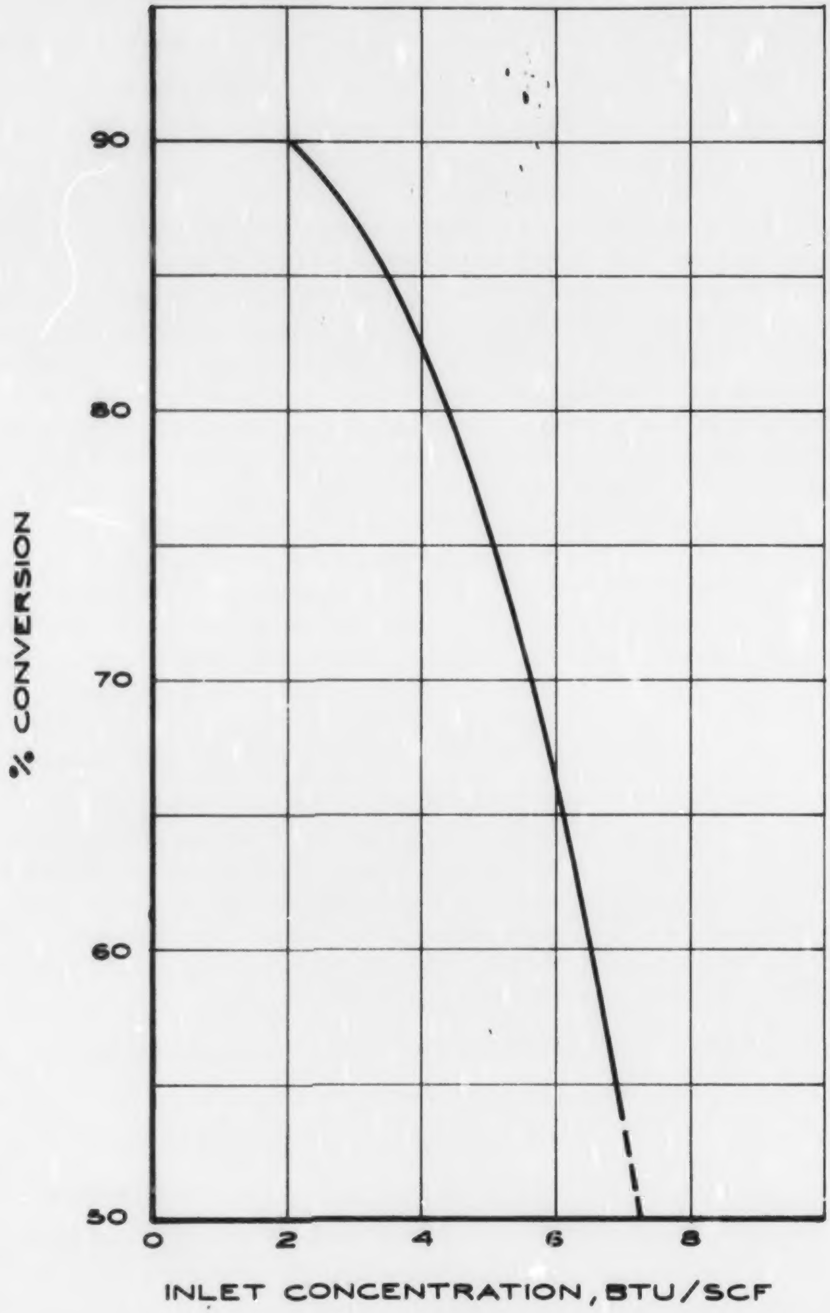
Frequently it is possible to identify specific materials which must be oxidized in order to conform to the prevailing air correction ordinances, or to good practice. For example, for closed kettles emitting a mixture of xylene and phthalic anhydride, one should consider the residence time-temperature curve for P.A. and select conditions which will give a 90% or better conversion of this material. As the xylene is less refractory than the P.A., this selection is "safe".

Often, however, it is not possible to chemically identify the specific compounds involved. In such cases, the emission must be treated on the basis of past experience or by using pilot afterburner equipment for field testing. Because the oxidation rates given are influenced by burner design, distribution in the combustion chamber, etc., it is wise to follow the recommendations of the manufacturer supplying the equipment rather than transfer data of this sort from one design to another.[29]

In general terms, a thermal afterburner consists of a preheat burner, a mixing device, and a residence chamber. The gas to be disposed of is first passed by and mixed with burner combustion products to preheat it to at least the reaction initiation temperature. The type of mixing device used is the single most important design feature in that it affects the amount of direct flame incineration

FIGURE 47

CONVERSION VS. INLET CONCENTRATION
AT
0.6 SEC. RESIDENCE TIME & 1350 °F OUTLET



that occurs and the temperature uniformity of the gases in the residence chamber.

As high as 20% of the gas can be mixed with and incinerated by the high temperature flame. This is a desirable effect in that it decreases the burner preheat fuel requirement and decreases the combustible load on the afterburner.

Gas flow and temperature uniformity out of a mixing device and into the residence chamber are important to assure that all the combustible is held at the proper temperature for the design time period. This effect is sometimes called turbulence, which is a misleading word. Uniform flow and temperature with or without turbulence is the important criteria. The importance of this variable is explicitly outlined in the *Afterburner Systems Study*, EPA Contract EHS-D-71-3,[27] and is quoted below.

> "Mixing of bypassed fume and hot combustion gases is the most crucial step in attaining good afterburner performance. Typically, afterburners are designed with ~.5 second total residence time. This time is nearly all required for this mixing step and many designs fail to complete the mixing in the distance (time) available. Some fume escapes without being raised to a sufficiently high temperature. To meet a performance specification (if possible at all) more fuel must be burned than would be needed if mixing were complete. Distributed burners are placed directly in the fume stream and divide the flame into many individual jets or lines of flame surrounded by fume. This subdivision greatly speeds the mixing process, and these burners are well suited to use oxygen from the fume for combustion. The use of outside air requires an additional 30 to 50% of the fuel to be burned to heat it to 1400°F. Distributed burners are subject to fouling, have somewhat limited turndown, aren't available for use with oil fuel, may be difficult to use with outside air, and have a few other potential drawbacks. Therefore, many afterburners employ discrete burners which give either long or short point sources of flame. The mixing problem is much more difficult since there is no subdivision at the burner. Internal baffles are required in the relatively short afterburner chambers utilized in available designs.
>
> Many designs stress "flame contact" in an attempt to mix fume and flame as rapidly as possible. This often leads to flame quenching and an increase in pollutants in the fume stream since, as was mentioned above, complete fume/fuel mixing gives a noncombustible mixture. Fuel should be burned as rapidly as possible and the hot gases should be mixed with bypassed fume. Pressure drop must be expended in achieving good mixing through baffles and/or a long chamber. Mixing will be faster when there is initial fume/flame subdivision."

A schematic illustration of a typical thermal afterburner and control system has been presented in Figure 48. As indicated on this Figure, most afterburners are equipped with heat exchangers to decrease the fuel requirements of the preheat burner. The burner fuel consumption is the major operating cost of thermal afterburners, and self-recuperative heat exchangers, except for very small flow rates or unusual circumstances, are an economic necessity with rapid payout. The use of

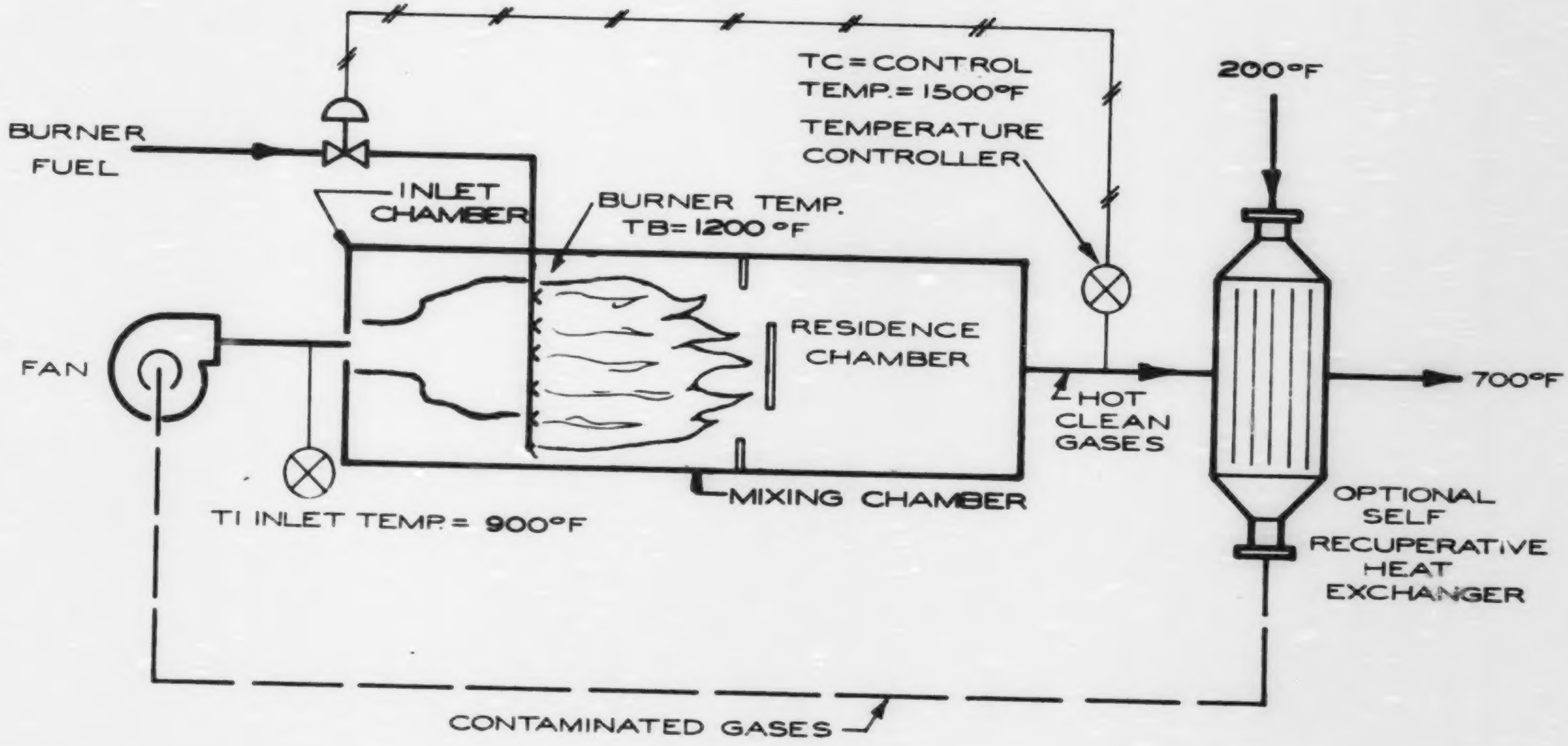


FIGURE 48

SCHEMATIC OF TYPICAL THERMAL AFTERBURNER AND CONTROL SYSTEM additional heat exchange, where possible, has become more attractive in recent times with the advent of fuel shortages and increased fuel costs.

Another technique commonly used to reduce operating cost through reduced fuel savings is preheating of the contaminated air with a raw gas or secondary air burner. This type burner utilizes the oxygen in the contaminated air for combustion of the natural gas.

This type of operation saves the cost of heating the combustion air and fuel consumption can be reduced about 30%. These burners, however, do not operate well at oxygen concentrations below 16% which would be the case for the emissions from a closed varnish or resin kettle or reactor. The maximum allowable fume concentration to the afterburner as set by most insurance companies is 1/4 of the lower explosive limit, or 13 Btu/SCF. This requires that the kettle exhaust be diluted sufficiently with air to raise the oxygen concentration above 16%.

As mentioned earlier, heat exchange is the most common type of fuel saving applied to thermal afterburners.

The type most often used is the self-recuperative type of exchanger which allows part of the heat in the effluent gas to be used for preheating the inlet gas before it reaches the combustion chamber. Gas-to-gas heat exchangers of this kind are generally supplied as a part of the thermal afterburner unit and are ordinarily available only from the manufacturers of equipment. Inherently, such exchangers are costly, and have a low heat transfer coefficient, 4 to 6 Btu/ft^2 — °F. Aside from the refractory regenerative type heat exchanger, most exchangers are of metal construction and have a hot gas or afterburner outlet limitation of 1500°F. The most common type in use is the shell and tube exchanger, and they are available in either parallel flow or countercurrent flow.

Parallel flow is most commonly supplied as a standard, especially where the fume load and outlet temperature are high. At high fume loads, there is a danger of temperature spiraling. At fume loads approaching 1/4 LEL, a 7.5% change in concentration will result in a temperature change in the residence chamber of 50°F. It is possible with sudden increase in fume loads to raise the afterburner outlet temperature above the control point which, via the heat exchanger, raises the inlet temperature above the burner's low fire control ability. The increased inlet, in turn, raises the outlet some more which, in turn, raises the inlet, and so on. Parallel exchangers having equal thermal flows on shell and tube side have a maximum thermal efficiency of 50% and are self-limiting with respect to temperature spiraling. They also have the advantage of running the lowest mean material temperatures, since the hottest gas is always exchanged with the coolest gas.

Countercurrent heat exchangers are much more thermally efficient for the same amount of heat exchanger area. They do run at higher material temperatures, however, and require more expensive materials of construction. They are also more susceptible to temperature spiraling when running at high fume rates. Because of this, a system designed around this type of exchanger should use a burner duty of at least 50°F. An afterburner heat exchanger system using a parallel flow heat exchanger is designed for a burner duty of at least 25°F. Burner duty in this context, means the temperature rise added to the fume stream by the burner between the heat exchanger outlet and the residence chamber inlet.

Rotary heat exchangers are available and will run at thermal efficiencies of 80%. They are of metal construction (321 SS) and are still limited to a maximum operating temperature of 1500°F. Their disadvantages are high initial and maintenance cost, as well as cross leakage. The cost of an 80% rotary ($84,000) is about double a 60% cross flow shell and tube ($47,000) for a flow of 12,000 SCFM. The rotary exchanger is still in the development stage and, along with its many operating problems, is limited to smaller sizes.

3. Catalytic Afterburners

While thermal afterburners bring about oxidation at concentrations below the limits of flame combustion, catalytic afterburners operate both below the limits of flammability and below the normal oxidation temperatures of the contaminants as well. The reaction is instantaneous by comparison to thermal oxidation and no residence chamber is required. Catalytic oxidation is carried out by equipment such as that illustrated in Figure 49. This particular arrangement provides an ideal location for the fan used in the system. Generally speaking, catalytic afterburner systems are the least costly when comparisons are made at the optimum level of heat recovery. Detailed installation and operating and maintenance costs for both catalytic and thermal afterburners are presented in Chapter 7.

While catalytic oxidation is attractive from an economic standpoint, several factors must be considered in selecting this form of waste gas treatment. Catalysts require regular maintenance in the form of periodic washing to remove atmospheric dust and dirt and, in the case of higher temperature cooking, to remove traces of particulates and other ash-like residue originating in kettle materials. In addition, it is necessary to reactivate the catalysts periodically. There are a number of materials, such as phosphorus, silicon and lead, known to shorten the active life of these catalysts. However, when the characteristics of the gas to be treated are suitable, catalytic oxidation is a highly satisfactory method for air pollution control.[27]

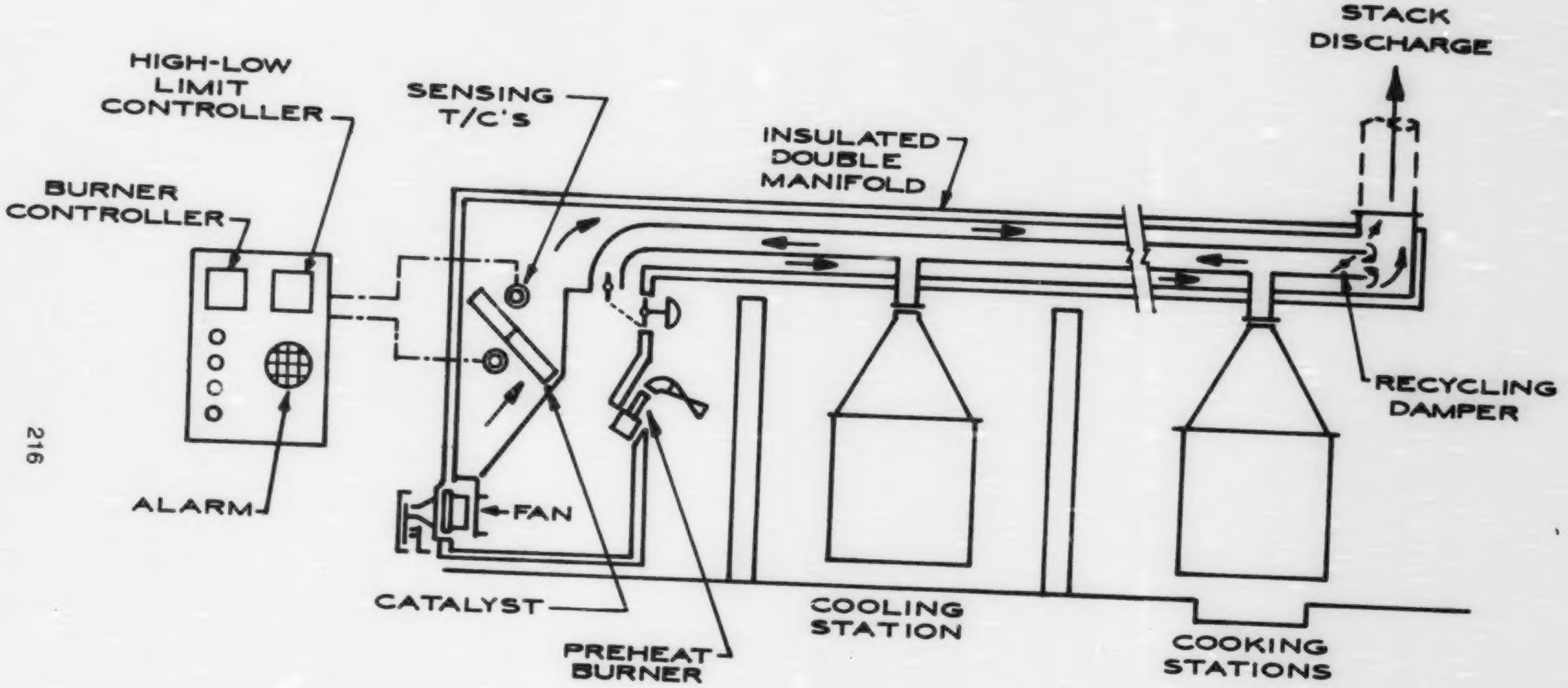


FIGURE 49

SCHEMATIC DIAGRAM OF A CATALYTIC OXIDATION SYSTEM FOR VARNISH KETTLES

Because catalytic units are not automatically functional when operated at design temperatures, they may not be approved for installation until means for ensuring adequate performance of the catalyst on a long term basis can be demonstrated.

As is the case for thermal afterburners, catalytic units can also operate at efficiencies in excess of 97% depending upon a number of operating variables. These conditions can be summarized as follows:

a. Type of Hydrocarbon — Reaction Rate
b. Quantity of Hydrocarbon
c. Type of Catalyst — Activity
d. Quantity of Catalyst — Space Velocity
e. Operating Temperature
f. Presence of Catalyst Suppressants or Poisons

Some hydrocarbons react faster or oxidize at lower temperatures than others. Relative reaction rate constants for various hydrocarbons in the presence of a precious metal catalyst are given in Figure 50.

As discussed earlier, the higher the hydrocarbon content of the exhaust stream, the greater the heat release, and the higher the temperature rise for an equal conversion efficiency. This is less of a problem than with thermal incinerators for two reasons. First, catalytic afterburners constructed of aluminized steel can sustain a temperature rise of 700°F, and units constructed of stainless steel can sustain temperature rises of 1,000°F. High temperature rises do not result in a lower average catalyst temperature or reaction rate since catalytic units are normally controlled on the catalyst inlet side.

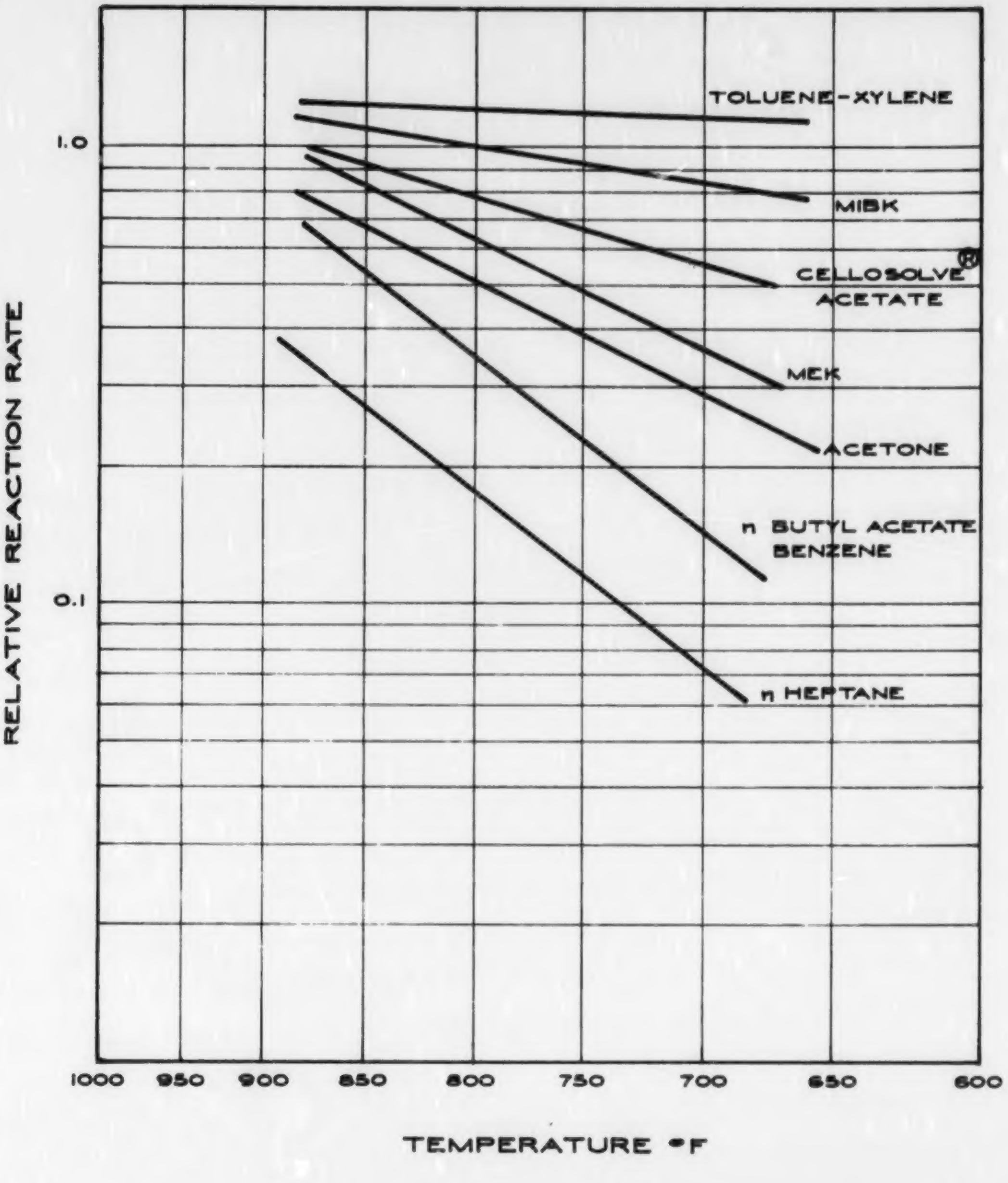
The catalysts in common use for oxidation reactions involved in stationary source control are metals of the platinum-palladium group. The only catalysts used in significant amounts for oxidation of trace hydrocarbons other than the platinum-palladium metals are merchandised in Europe and consist of cobalt, copper, and chromium oxides incorporated into a ceramic substrate.

Oxidation, which is of primary concern in air pollution control, generally takes place only over metal catalysts, and is inhibited by acidity in the support. The kinds of metals that are capable of bringing about oxidation reactions are listed in order of the frequency of their utilization.

a. Platinum and Palladium
b. Nickel, Cobalt, Iron, Vanadium
c. Silver and Copper
d. Tungsten, Chromium, Molybdenum

FIGURE 50

CATALYTIC OXIDATION RATES FOR SOLVENTS



Because the reactions take place only on the surface of the active metals, very small crystallites are generally preferred as they provide a much larger surface area per unit weight of precious metal.

The available surface area of the substrate may be a critical factor, but is more likely to be of marginal importance in oxidation reactions. The substrate surface area must be sufficiently adequate that the active metal crystallites do not pile up one above the other and thus limit the surface area exposure to the bulk gas stream.

In general, the metal ribbon catalysts have very little substrate surface area. The spherical catalysts ordinarily have extremely large surface areas associated with a "micropore structure". Generally the area is measured in square meters per gram of material with values frequently as high as 250 square meters per gram. The ceramic honeycomb materials manufactured by duPont, Minnesota Mining and Manufacturing and Dow Corning have somewhat greater superficial surface area than do the metal ribbon catalysts, but have substantially no micropore area as the spherical supports have.

Generally, catalysts of higher activity can be produced from a porous catalyst support of high surface area than from a metal substrate. However, for ordinary applications at high temperatures the precious metal located away from the outside surface of the spherical catalysts is not used effectively, and the advantages of the porous bases seem to lie only in their having more superficial surface area than it is convenient to pack into the same volume with the metallic ribbons or ceramic honeycombs.

Even though the oxidation reaction over a catalyst is instantaneous in comparison to thermal oxidation reaction time, the more catalyst it contacts the greater the conversion rate. The disadvantages of adding additional catalyst in an afterburner are increased pressure drop across the catalyst bed and higher capital cost. For this reason, the expected operating temperature and type of hydrocarbon must be considered when sizing the catalyst volume for a catalytic afterburner.

The effect of operating temperature on catalyst activity is illustrated on the previously presented Figure 50. Basically, catalysts function by altering the rate of a reaction. If a gas contains species A and B which react to produce C, such that there is substantially no reverse reaction of C decomposing into A and B, we write the equation:

$$A + B \rightarrow C$$

For flow processes, if we assume steady conditions of a gas stream passing through a container with good uniformity across any given cross-section, the concentration of A, B, and C will vary with time as an element of the flowing fluid moves through the reactor, or with distance, in that time and distance into the reactor are interchangeable for steady-state conditions. We will expect the concentration of A or B to drop off and can define the rate of disappearance of A as follows:

$$\frac{dA}{dt} = -r$$

where, $\frac{dA}{dt}$ = rate of disappearance of A, mol/sec.

For a normal gas phase reaction, the rate of disappearance of A will vary with the concentration of A, the concentration of B, and the temperature. If we assume that the reaction is controlled primarily by the concentration of A, as in the case of burning traces of hydrocarbons in an air stream, the equation becomes:

$$\frac{dA}{dt} = -ka$$

where,

k = reaction rate constant

a = concentration of A in mols/liter

The solution to this equation is:

$$\frac{a}{a_o} = e^{-kt}$$

where:

a_0 = initial concentration of A

which simply says that the concentration of A will drop off exponentially with time, or with distance as the flowing stream moves down the reactor. If it does so, the reaction is defined as a first order reaction with respect to A. In order to predict the course of a reaction such as this, all we need to do is know what k will be. Generally speaking, for any given reaction, k is a function only of temperature.

For most purposes, we may use:

$$k = (A)\,(e)^{\frac{-Eo}{RT}}$$

where

A = collision coefficient

Eo = energy of activation, Btu/lb mol

R = universal gas constant = 1.92 Btu/lb mol °R

T = temperature, °Rankine

The constant A is a measure of the likelihood of a molecule of A bumping into one of the more plentiful B molecules. The exponential function measures the probability that a collision of A and B will have sufficient energy to bring about a reaction. The energy of activation determines the temperature level to which the mixture must be raised before the reaction will proceed at a significant rate.

The function of the catalyst is to reduce the activation energy, and bring about reactions at a lower temperature than can be accomplished by thermal means alone.

The reaction rate constant plot is ordinarily straight only over a relatively narrow temperature range. At low temperatures, the catalyst surface tends to be fully occupied by gases and the reaction rate may be limited by the availability of unoccupied surface. For example, at low temperatures, oxygen adsorbs on platinum surfaces almost to the exclusion of methane or other light hydrocarbons. In the middle range, the rate at which the reaction occurs on the metal surface is limiting, and adsorption and desorption occur with relative ease.

At high temperatures the catalyst surface is likely to remain relatively free of adsorbed gases, and the difficulty of adsorbing the reactants onto the surface limits the reaction curve. Figure 51 indicates the shape of the reaction rate curve over these three ranges.

As mentioned earlier, oxidation reaction rates of hydrocarbons in the presence of catalysts are significantly higher than those encountered in thermal oxidation. A comparison of thermal and catalytic reaction rates for maleic anhydride is presented in Figure 52. From this comparison it can be seen that catalytic oxidation is instantaneous by comparison at a significantly reduced temperature.

Since catalytic units can operate at relatively low temperatures, they can be designed with inner walls of aluminized carbon steel. This low construction cost offsets the high cost of the catalyst contained in the afterburner and overall capital costs of catalytic afterburners run about the same as other types of afterburners.

Heat exchangers are also frequently used as heat recovery devices with catalytic units. They may also be designed of carbon steel or aluminized carbon steel. Being relatively less expensive, they have payouts equivalent to those exchangers used with other types of afterburners. The design of heat exchangers for catalytic units should follow the same rules outlined earlier for thermal afterburners.

While the scientific basis of catalysis is not as clear as that of many of the other industrial

FIGURE 51

REACTION RATE CONSTANTS
FOR
LOW, INTERMEDIATE, AND HIGH TEMPERATURES

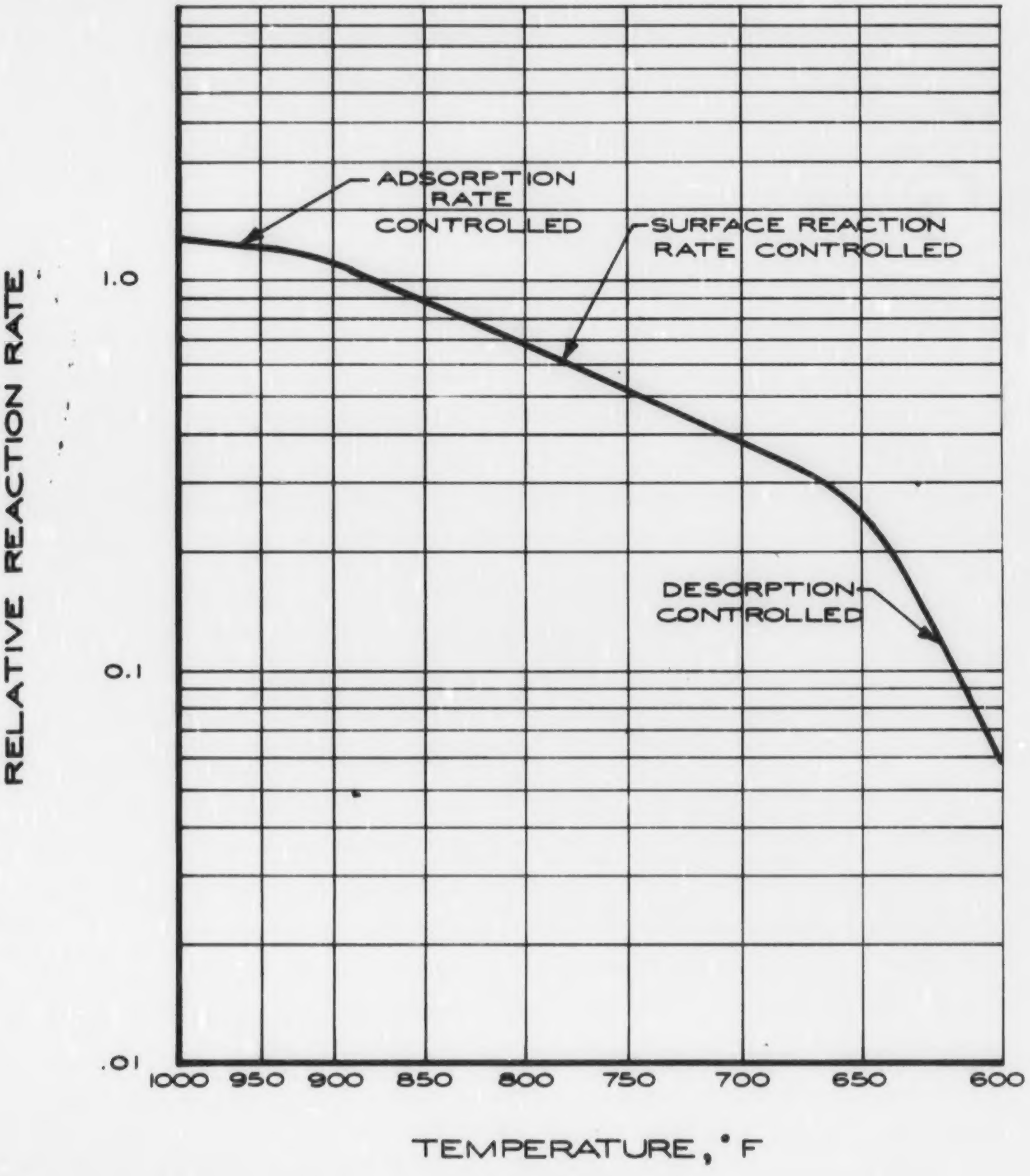
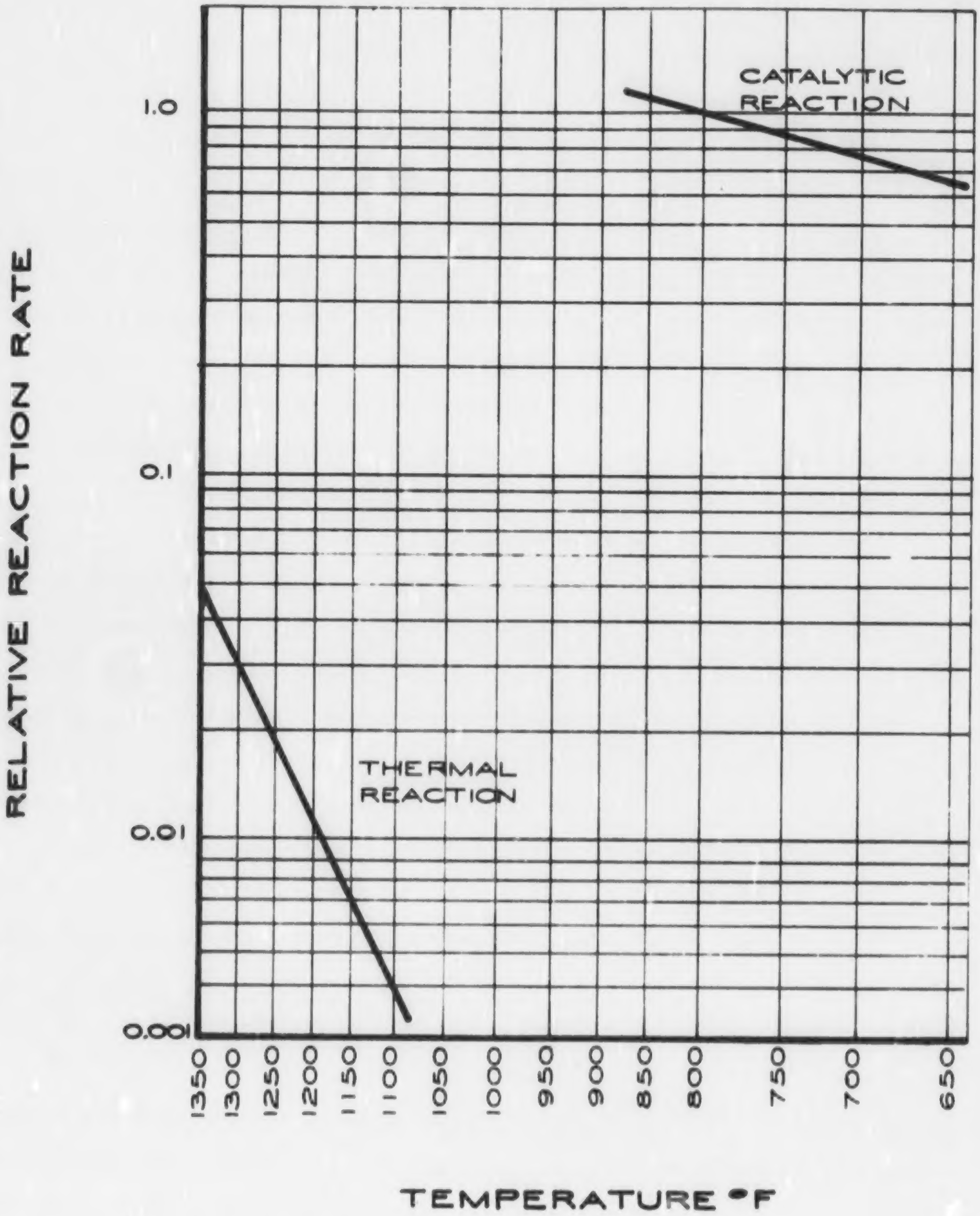


FIGURE 52

COMPARISON OF THERMAL AND CATALYTIC REACTION RATES FOR MALEIC ANHYDRIDE



arts, the thermodynamics are sufficiently well known that catalysts can be characterized with good success. Catalytic afterburners have been widely used in the past for the oxidation of paint solvents, and emissions from open and closed varnish kettles. Most new installations, however, are using thermal afterburners. It is anticipated that this trend will reverse itself in the near future due to the ever increasing shortage of fuel.

II. DESCRIPTION OF EMISSION CONTROL OTHER THAN BEST CONTROL

A. Scrubbers

Wet scrubbers can be relatively effective for the control of phthalic anhydride particulate and very heavy organics if properly designed. Efficiencies will run between 85 to 95% at pressure drops ranging from 4 to 8 in. w.c. They have little effect, however, on solvents and other light and medium weight organics. For the type of material which was measured in the emission curves given in Chapter 1, scrubbers are not suitable control devices. Source test engineers from air pollution equipment manufacturers have reported that the typical scrubber installation removes at most 10% of these contaminants.

Water treatment and/or disposal of waste can be expensive in many cases. With increasing emphasis on water pollution control, treatment of effluent streams will be required in more and more localities. The use of chemicals, e.g. permanganate, in the scrubbing solution further increases cost.

Relatively low cost, as well as safety considerations, have traditionally been the primary advantages of scrubbers in the resin industry. While it will probably cost more to operate scrubbers in the future than in the past, their use as pre-treatment devices to remove phthalic and add a measure of safety before incineration may still be desirable, particularly in fusion cooking.

B. Vapor Condensation

The use of refrigerated condenser systems has sometimes been proposed as an air pollution control device. A system of this type is in use in at least one location, the Sherwin-Williams plant in Oakland, California. Sherwin-Williams has supplied design and operating information for their system so that it can be included in this report.

A schematic of the system is shown in Figure 53. Four kettles are controlled by this system. Kettles A and B are conventional Dowtherm® heated kettles used for alkyds and polyesters. Kettle A contains a reflux condenser as well as a final water cooled condenser while Kettle B has only the final condenser. Kettle C is steam heated and is used only for cutting resin into solvent. Kettle D

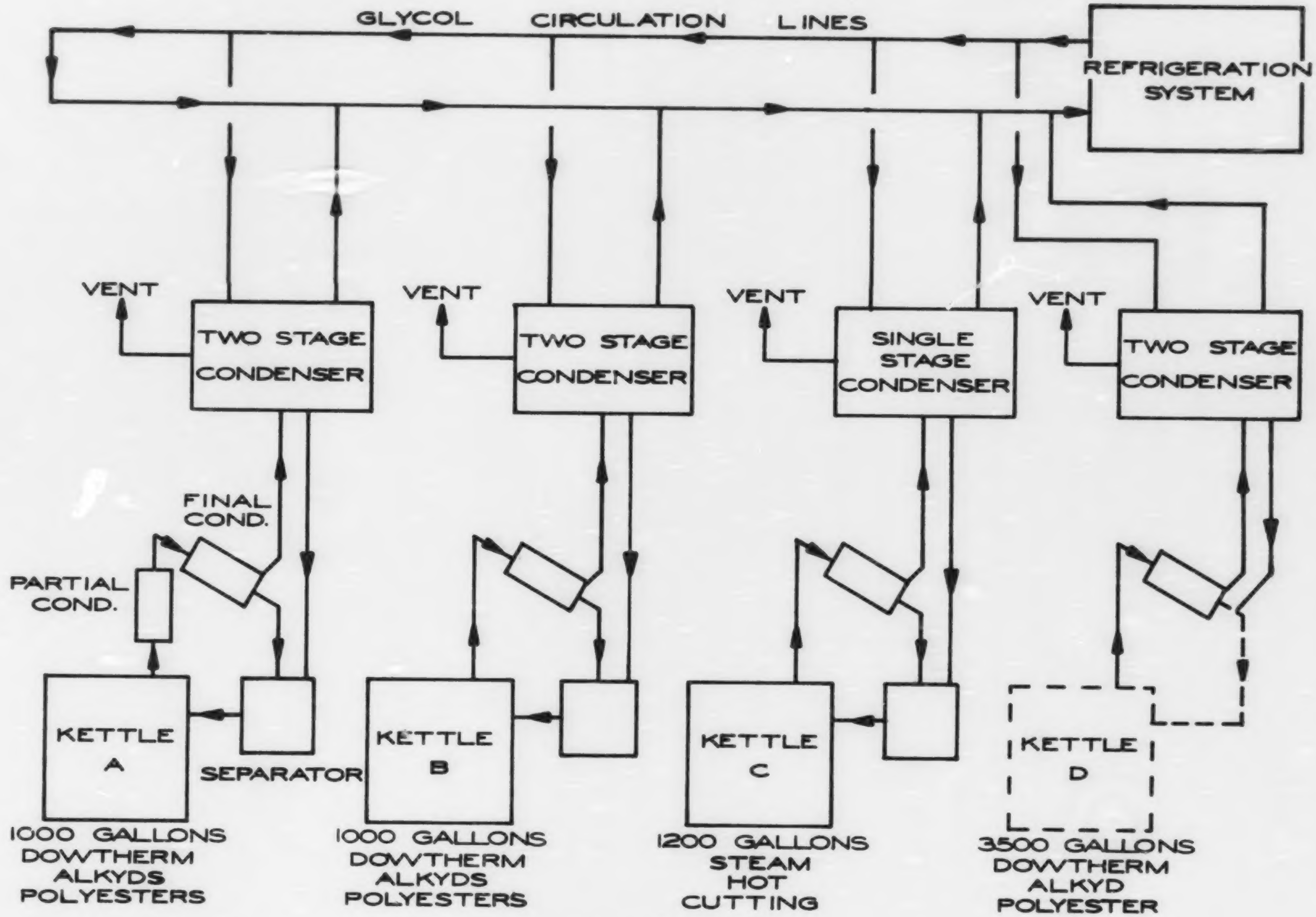


FIGURE 53
REFRIGERATED CONDENSER SYSTEM FOR CONTROL OF RESIN KETTLES

is Dowtherm® heated and used for alkyds and polyesters. While the mechanical details of D are considered proprietary, it does contain a water cooled final condenser.

The exhaust streams from Kettles A, B and D are controlled by identical two stage refrigerated condenser systems. Kettle C requires only a single stage. A separate condenser system is used for each reactor but all condensers are supplied by a single refrigeration system. The refrigerated condensers are used only during solvent cooking.

The refrigeration system is shown in Figure 54. All temperatures shown are to be considered nominal only. They can vary from run to run over a range of several degrees. Two separate glycol circulation systems are employed. The "sub-zero" loop is cooled directly by the refrigeration system. A branch of this loop is used in the cold side of a heat exchanger to cool the "40°F" circuit.

The design basis for this system requires a refrigeration duty of 54,800 Btu/hr. Almost 1/3 of this is due to heat gained in the transfer lines. Two 5 ton refrigeration units are provided. Only one operates at a time except when cooling down the entire system at start-up. The design was based on the assumption that all kettles are operating simultaneously. It was further assumed that each kettle exhaust rate can run as high as 15 cfm noncondensibles and that this gas is saturated with solvent at the operating temperature of the final condenser (~100°F). The refrigeration unit has sufficient capacity to handle a continuous discharge exhaust at that level even though the kettles are operated in such a way that the inert gas flow is intermittent. Furthermore, measurements by Sherwin-Williams have shown that the final condenser vent averages only 50 to 60% saturation for these kettles. The 54,800 Btu/hr, then, represents a worst case situation.

A schematic of one of the two stage condenser systems is shown in Figure 55. The exhaust gas from the water cooled condenser flows to the shell side of the first stage condenser which is cooled by the "40°F" glycol. From there it flows to the second stage condenser which is operated at sub-zero. The majority of the condensate is collected in the first stage.

On occasion, the second stage condenser accumulates an excessive amount of frost. To alleviate this, a system of four-way valves is provided which enables the streams to be switched. In this case, the kettle exhaust flows first to the second stage which is now cooled by the "40°F" glycol, and so on.

Kettles A, B and D use systems identical to that shown in Figure 55. Kettle C uses a single stage condenser cooled by the sub-zero circuit. Frost formation is not a problem here since no water is formed in this kettle.

The results of two tests, conducted by an outside consultant, have been supplied by Sherwin-

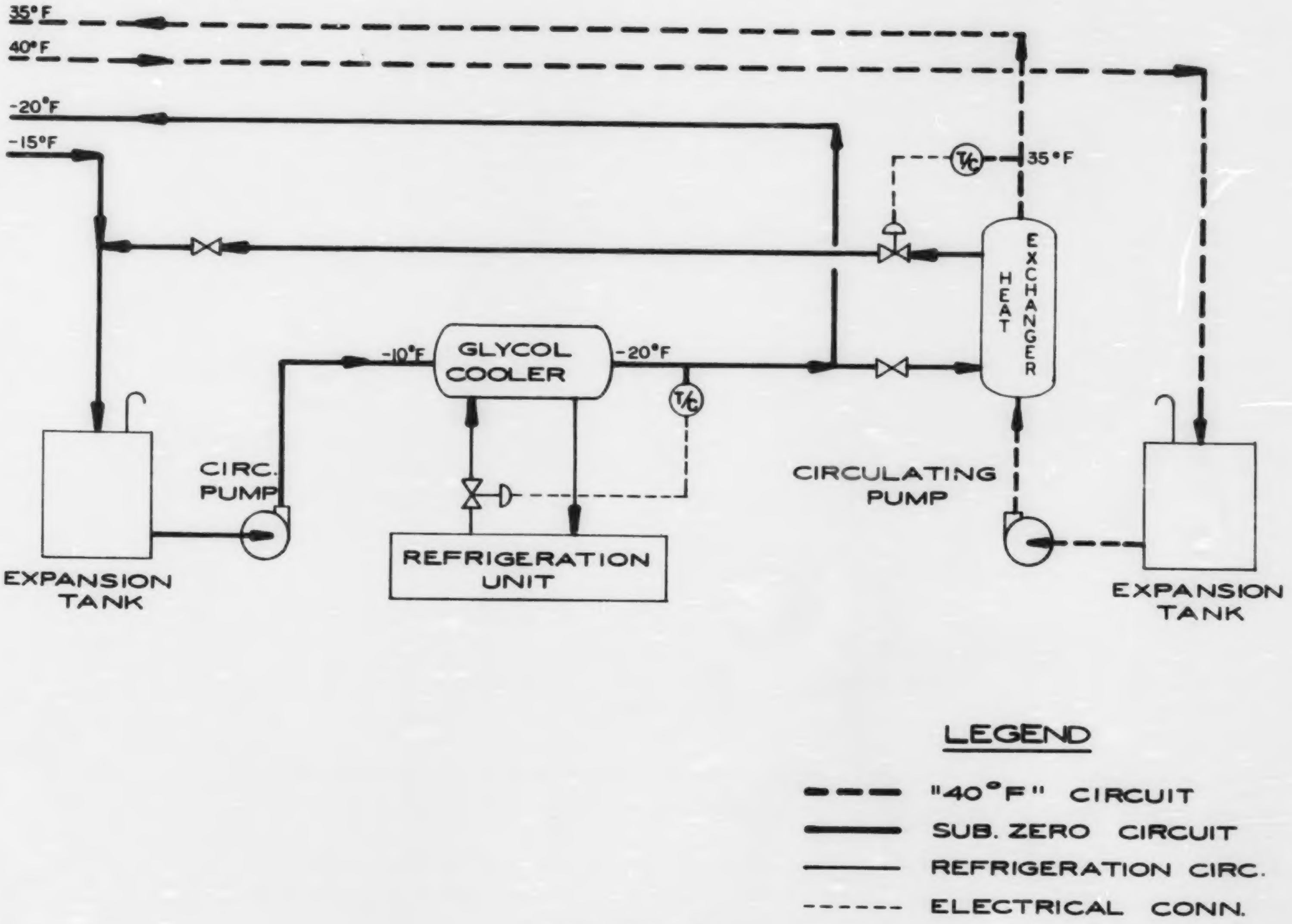


FIGURE 54
REFRIGERATION SYSTEM

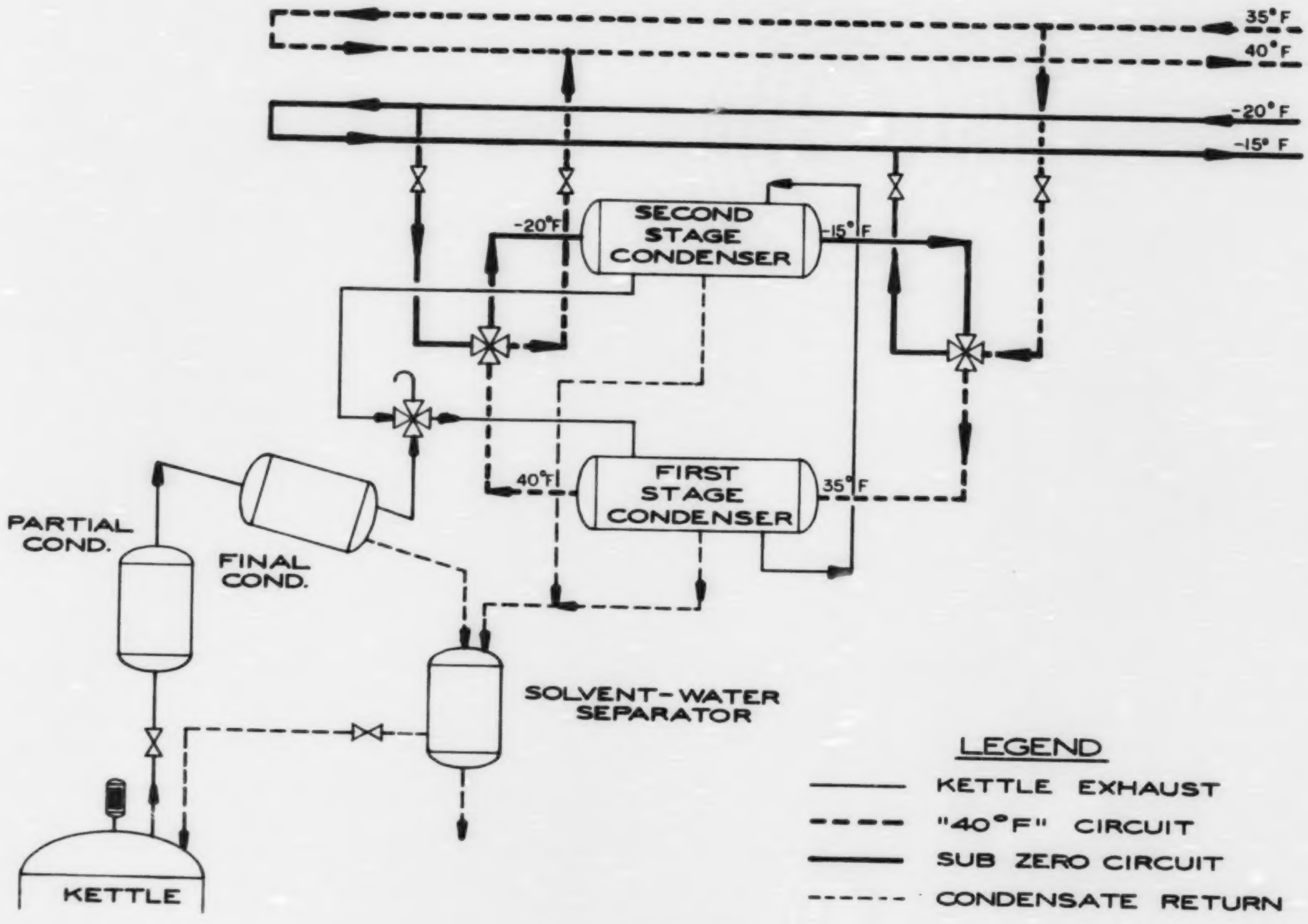


FIGURE 55
TWO STAGE CONDENSER SYSTEM

Williams. A tall oil fatty acid alkyd cook was conducted in Kettle A by the solvent process. Testing and observation was done over the entire cooking cycle even though no inert gas flow was used until the last 80 minutes. The results are presented in Table 50. No condensate was collected until the stripping operation was started. Inert gas rate during stripping was about 8 SCFM.

Light organics were determined by GC analysis of gas samples collected in sample bulbs at the second stage condenser vents. Heavy organics were determined by GC analysis of gas samples absorbed in silica gel at the second stage condenser vent and by GC analysis of the condensate collected in the two condensers.

A solvent process polyester cook was conducted in Kettle D. The results of this batch are presented in Table 51. The inert gas flow was turned on for a short period of time during the cook and then turned off. Figure 56 shows cumulative gas vented and cumulative condensate formed during this run. The results from this run are not typical of those for Kettle D. The large volume of condensate collected during the fourth hour was due to improper operation of the water cooled condenser during this time. Consequently, a higher than normal amount of material passed the water cooled condenser. Inert gas flow rates of about 6 SCFM were observed in the early part of the run.

Examination of Tables 50 and 51 show that for the alkyd cook on Kettle A, the condenser system was 84.6% effective on total organics and 85.7% effective on reactives, while for the run on Kettle D, the efficiencies were 98.4% and 98.9% respectively.

The extremely high efficiencies in the second case are probably due to the fact that the majority of the condensate was collected while the inert gas flow was negligible. During this period the vapor entering the first stage condenser was almost 100% condensible. This represents an optimum situation from the standpoint of condenser efficiency provided adequate refrigeration duty is available.

In any event, the systems performed well enough in both cases to bring the kettles into compliance with Bay Area APCD Regulation 3 which requires 85% reduction in reactive organics.

During the test period while both the previously described cooks were taking place, power consumption by the compressor and glycol circulation pumps ranged from a low of 3,720 watts to a maximum of 9,150 watts with a time average value of 7,790 watts. The reason for the variation is that the compressor cycles on and off as required to maintain the coolant temperature. This represents the primary operating cost of the system. No additional manpower is required as this system can be attended to by normal staff. The system has not been in operation for a sufficient

TABLE 50

KETTLE A – ALKYD COOK

	First stage inlet lb/batch	First stage condensate lb/batch	Second stage condensate lb/batch	Total Emission to atmosphere lb/batch
Light organics (C_5, and less)	0.0007	–	–	0.0007
Toluene	0.255	0.080	–	0.175
Ethylbenzene	2.125	1.910	0.048	0.167
Hexane	0.016	Tr.	–	0.016
Benzene	0.003	Tr.	–	0.003
Light carbonyls (as HCHO)	0.009	–	–	0.009
Total organic	2.4087	1.990	0.048	0.3707
Water	0.120	0.120	–	–
Total	2.5287	2.110	0.048	

Gas vented total = 641 SCF inerts

Average emission rate,

before control =0.189 lb/hr organics (First stage inlet)

after control = 0.0291 lb/hr organics (Second stage vent)

Test period = 12.75 hr

% reduction, total organics = 84.6%

% reduction, reactives = 85.7%

TABLE 51

KETTLE D — POLYESTER

	First Stage Inlet, lb/Batch	First Stage Condensate, lb/Batch	Second Stage Condensate, lb/Batch	Total Emission to Atmosphere lb/Batch
Light organics (C_5, and less)	0.001			0.001
Toluene	7.838	6.95	0.785	0.103
Ethylbenzene	5.375	4.80	0.565	0.010
Hexane	1.196	0.85	0.240	0.106
Benzene	0.339	Tr.	0.328	0.011
Light carbonyls (as HCHO)	Tr.	—	—	—
Total organic	14.749	12.60	1.918	0.231
Water	1.663	1.63	0.033	
Total	16.412	14.23	1.951	

Gas vented total = 125 SCF inerts

Average emission rate, before control = 1.55 lb/hr organics (first stage inlet)

Peak emission rate, before control = 52 lb/hr organics (first stage inlet)

Average emission rate, after control = 0.0243 lb/hr (second stage outlet)

Test period = 9.5 hr

% reduction, total organics = 98.4%

% reduction, reactives = 98.9%

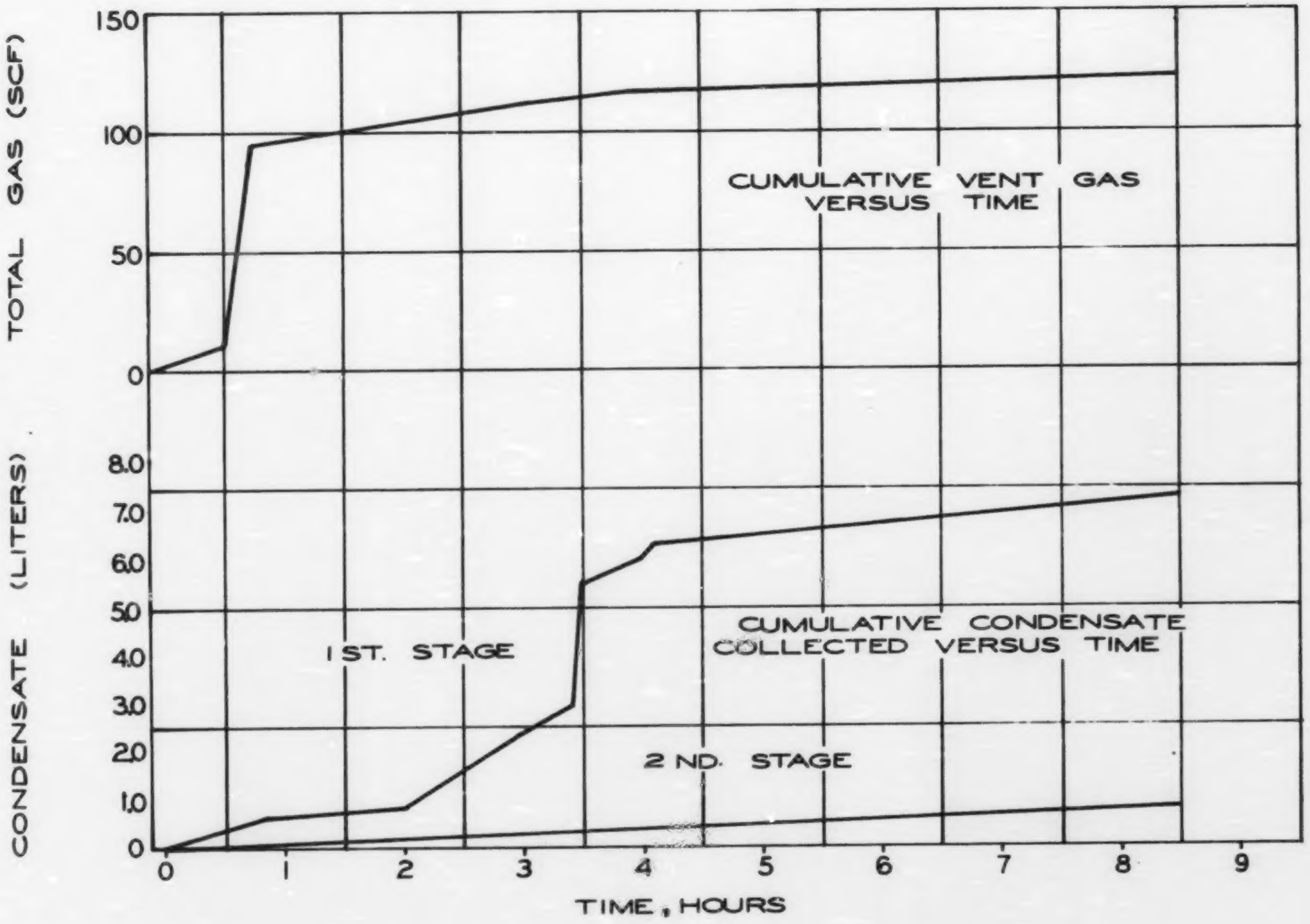


FIGURE 56
EMISSION CHARACTERISTICS - KETTLE D

length of time to determine equipment repair and replacement requirements.

The capital cost of the entire emission control system in 1971 was about $90,000. Estimated capital cost for a thermal afterburner system, without heat exchange, is $32,000. With a 42% heat exchange, the capital cost would be about $50,000.

Thermal oxidation has a substantial advantage as far as initial cost is concerned. The operating cost advantage probably lies with the condenser system, though insufficient information is available to determine the extent of this at present.

The condenser possesses some features which are attractive in spite of its higher initial cost. It is an inherently safe control device since no flame or high temperatures are involved. This is demonstrated by its performance on the polyester cook in Kettle D described earlier. As mentioned before, this cook was not typical in that the water cooled condenser failed to operate properly for a time. During this period, instantaneous emissions ran as high as 52 lb/hr as compared to an overall average of 1.55 lb/hr. Such a sudden increase over the expected rate could be disastrous for an afterburner installation unless elaborate safety devices were installed. The condenser system handled the increased emission rate without problem.

On the other hand, the condensers are not suitable for use when fusion cooking. Also, the efficiencies are high only when the gas stream is very concentrated in condensibles. This means that condensers are impractical for controlling emissions from other parts of a paint plant such as mixing tanks, filter presses, etc. An afterburner installation can be designed to handle both resin kettles as well as other sources simultaneously. Perhaps the ideal solution would be to control the kettles with refrigerated condensers, where safety is a prime consideration, and to control the other sources by collecting their emissions in hoods and ducts and then incinerating the fumes.

III. METHODS OF CONTROL OTHER THAN ADD ON EQUIPMENT

As is the case with most industrial operation, it is possible to reduce and sometimes eliminate emissions of pollutants by modification of the manufacturing operation. Various approaches of this type, applicable to this industry, are listed below.

A. Raw Material Substitution

Raw material substitution in many cases can provide an excellent and inexpensive method of emission reduction for the manufacturer. Unfortunately, this may not also be true for the user since raw material substitution can lead to both higher prices and poorer quality. These potential problems should be remembered when considering this method of emission control. An example, unrelated to air pollution, of product degradation in this industry caused by raw material substitution is the removal of mercury fungicides and lead drying agents. Industry spokesmen have indicated it may be as long as three years before an equal raw material substitution may be found and the quality of paint returned to its former position.

1. Solvents — As discussed earlier, the major emission in the paint manufacturing industry comes from the solvents used in the various production operations. The quantity of emission is small, however, when compared to that emitted by the final user.

Current regulation in most states allow for significant emissions of the non-photochemically reactive solvents described earlier in Section I. Because of this there has been significant pressure to develop paint products with a non-solvent system, or with a non-photochemically reactive solvent system.

Significant progress has been made by the paint industry in the use of exempt systems through the development of the water emulsion paints. These products have been developed without sacrifice of quality or increased cost.

The current development of dry powder systems also appears to offer these same advantages and may result in a significant reduction of solvent emission from both production and application of paint.

Another technological development which has great potential in reducing solvent emissions, particularly by the user, is the formulation of water reducible industrial coatings. Heretofore, the use of water based coatings has been restricted almost exclusively to trade sales products. In the opinion of some experts, use of such industrial coating systems will come to fruition before powder coatings.

Use of high solids systems is a further area for potential improvement. The net result of this approach is to reduce the amount of solvent present per unit coverage of the applied coating. Consequently, solvent emissions by the user will be reduced.

There has also been a significant switch in the industry to non-photochemically reactive solvents; and, as might be suspected, this has lead to a reduction of objectionable emission by both manufacturer and user.

It appears that in many cases, either singly or in combination, these changes in the solvent system paints have resulted in either or both a higher price product or a poorer quality product. Some paint manufacturers feel it would be less expensive, overall, for their customer to apply pollution abatement to existing solvent emissions than it would be to pay the additional product cost of special paint solvent systems that are currently exempt. This, coupled with possible poor product quality and the likelihood that these solvents may not be exempt in the future, may make this raw material substitution a poor choice.

2. Pigments and Other Solids — The quantity of pigment emission can be reduced by the use of liquid slurries, which eliminates the dusting problem associated with handling of the bagged solid products. The use of water slurries of TiO_2, currently being practiced by many manufacturers, is a good example of such a raw material substitution. This substitution, as well as can be determined, will not result in additional cost, providing the usage level approaches 500 tons/year.

The use of liquid phthalic anhydride in resin manufacturing can also result in reduced kettle emissions. Introduction of PA into the kettle (as a liquid) eliminates the necessity of evacuating the kettle when this material is loaded as a solid through the hatch door. As described earlier, significant PA and solvent emission occur during this loading period.

The disadvantage to the use of liquid PA is the potential for emissions from the heated PA storage tank. This can be easily avoided, however, by venting the tank through a water jacketed vertical condenser with provision for admitting steam to the jacket. The tanks are blanketed with inert gas during storage with the appropriate provision for pressure and relief control. During filling the condensers remove PA vapors which can later be melted off and run back into the tanks.

B. Changes in Process or Operating Conditions

As discussed many times, there are two major types of resin cooking, solvent and fusion. In the solvent cooking process it is possible to maintain a substantially closed system by:

1. Not using sparge gas
2. Use of adequate condensers
3. Use of liquid polyols and acids
4. Use of proper unloading or transfer methods

Operations in this manner can almost completely eliminate emissions from this process. Continued development of closed kettle cooks is probably the most significant process and operating change that can be effected.

IV. PERFORMANCE OF CURRENTLY USED METHODS OF EMISSION REDUCTION

A Performance Data

Data describing the control efficiency of the various air pollution control devices currently being used by the paint and varnish industry is presented and discussed below. The data was gathered from the questionnaires used in this study, industry measurement not reported in the questionnaires and source testing conducted by the EPA.

1. Scrubbers — Scrubbers are frequently encountered in the paint and varnish industry. Simple spray towers are usually installed as part of closed resin kettle systems. As discussed in Section I, these are not considered pollution control equipment for the purpose of this report. Some performance data for these devices has been reported in the questionnaires and will be discussed below.

Scrubbers which qualify as air pollution control devices in the present context have also been reported in the questionnaires. The reported data for these devices has been described in Tables 52, 53, and 54.

These are predominately spray type scrubbers. Either plain water or water to which some chemical (e.g., caustic) has been added is used as the scrubbing liquid.

The efficiencies of these devices are reported in the questionnaires to range from 50% to 99% with practically all at 90% or better. Those who report efficiencies for spray towers which serve as process equipment generally claim efficiencies in excess of 90%.

The accuracy of these reports would seem to be questionable. The efficiency of a well designed scrubber could be good on relatively large particulate or on readily condensible organics. On small particulates or relatively volatile organics, the types of scrubbers generally reported would probably be ineffective. They are inherently limited where volatile, non-soluble contaminants are concerned. Aside from this problem, they also frequently violate the opacity regulations of most states.

Furthermore, it appears that in many cases an arbitrary number was picked for efficiency rather than a number based on actual measurements. Often, the inlet and outlet loadings were unknown yet a very high efficiency was claimed which seems contradictory.

If large amounts of condensible materials are emitted from a reactor, actual tests could indicate good efficiency. This could lead to a false sense of security, however, if the analytical technique ignores the noncondensibles. As reported in an earlier section, actual measurements have been performed on the noncondensible fraction of the emissions. Levels as high as several hundred thousand parts per million (CH_4 equivalent) have been measured. It was further found that the typical scrubber was at best 10% effective on these emissions.

2. Afterburners — Tables 54 and 55 summarize the questionnaire data reported for thermal and catalytic afterburners. Efficiencies for thermal afterburner are reported from "poor" to "excellent". Where a numerical value is given, it is always reported in excess of 90%. On the whole, these values are probably somewhat more reliable than those given for scrubbers. The inlet loading must generally be known for design and safety purposes and it is possible to estimate the effectiveness

TABLE 52*

TYPE 1 PLANTS

AIR POLLUTION CONTROL — LOADING MILLS, ETC.

FABRIC FILTERS

Paint Production MM gal/yr	Number of Devices	Total Gas Flow, SCFM	Air to Cloth Ratio
6.4	4	1,000	6.1
2.6	1	—	—
1.0	1	—	—
5.6	4	6,200	3.5
1.2	1	3,600	4.5
4.3	7	18,000	3.0
2.6	3	5,362	7.7
3.0	1	3,250	4.2
2.4	14	18,620	7.0
0.1	1	—	—
1.9	1	1,071	7.1
14.9	1	—	4.0
8.6	4	12,700	6.2
8.2	1	5,370	2.6
5.6	3	—	—
1.0	1	—	—
0.7	3	1,155	7.7
1.0	1	2,000	6.7
2.4	2	2,600	3.0
2.7	1	2,058	18.3
8.3	1	—	—
8.7	1	15,000	2.9
1.1	1	6,000	2.6
1.0	4	—	—

*Questionnaire Data

TABLE 52 (Continued)

SCRUBBERS

Resin Production MM lb/yr	Number of Devices	Total Gas Flow, SCFM	Efficiency	Type
0.4	1	—	—	Wetted baffle
2.8	1	2,500	—	Water spray
3.0	1	4,500	99%	Roto-clone
1.2	1	—	—	Water spray
14.9	1	9,610	95%	— —
2.4	2	6,000	—	Spray
3.6	1	—	—	— —

TABLE 53*

TYPE 1 PLANTS

AIR POLLUTION CONTROL — REACTORS AND KETTLES

SCRUBBERS

Resin Production MM lb/yr	Number of Devices	Gas Flow (cfm)	Efficiency**	Type	Operating Cost ($/year)
1.9	1	—	—	—	—
11.1	4	—	—	—	2,000
0.0	1	—	—	—	—
20.0	1	—	—	$KMnO_4$	—
0.5	3	—	90%	Spray	15,340
5.7	1	134	50%	—	—
33.7	2	—	—	—	—
20.7	1	—	—	—	—
5.4	1	15	85%	—	2,600
16.4	3	—	—	Caustic	15,400
0.3	3	600	99%	Caustic	175,000
17.6	5	500	98%	—	13,300
2.9	2	—	—	—	—
16.0	3	2,500	90%	—	—
3.5	2	1,180	—	Cyclone	1,1700

*Questionnaire Data

**See comments in text concerning reported efficiencies.

TABLE 54*

TYPE 3 PLANTS

AIR POLLUTION CONTROL — REACTORS AND KETTLES

AFTERBURNERS

Resin Production MM lb/yr	Number of Devices	Type	Total Gas Flow (cfm)	Temp. (°F)	Res. Time (sec.)	Efficiency	Operating Cost ($/year)
22.3	1	Thermal	31,000	1,400	0.42	90%	–
3.8	1	Thermal	5,000	1,200	1.0	–	–
64.5	1	Catalytic	250	850	N.A.	95%	–
2.7	1	Catalytic	2,600	600-1,100	N.A.	95%	3,094

SCRUBBERS

Resin Production MM lb/yr	Number of Devices	Total Gas Flow (cfm)	Efficiency**	Type	Operating Cost ($/year)
20.0	1	65	90%	–	14,000
36.0	3	195	90%	–	64,000
3.3	1	48	90%	–	2,120
1.1	1	2,200	92%	–	1,785
20.8	2	–	–	Caustic	50,000
17.0	1	50	–	Spray	12,500
38.0	1	530	90%	Oil	–
2.5	1	4,000	–	–	900
20.0	1	–	–	Caustic (batch)	900
80.0	1	100	–	Cold Acetone	3,000

*Questionnaire Data

**See comments in text concerning reported efficiencies.

TABLE 55*

AIR POLLUTION CONTROL — REACTORS AND KETTLES

THERMAL AFTERBURNERS

Resin Production MM lbs/yr	Number of Devices	Gas Flow (CFM)	Temp. (°F)	Res. Time (Sec)	Efficiency	Operating Cost ($/Year)
8.2	1	2,000	1,500	0.5	98%	10,000
38.5	1 (flare)	4,200	1,800	2.4**	—	—
1.9	1	2,000	1,200	2.1	Excellent	—
10.6	1	7,000	1,100	2.0	Fair	—
0.3	1	1,200	1,500	—	99%	1,800
0.2	1	500	1,400	0.3	Excellent	370
0.0	1	920	1,200	—	—	267
3.5	1	10,000	1,300	0.5	Poor	30,600
20.7	2	—	1,200	—	—	—

CATALYTIC AFTERBURNERS

Resin Production MM lbs/yr	Number of Devices	Gas Flow (CFM)	Temp. (°F)	Efficiency	Operating Cost ($/Year)
1.2	1	1,200	1,200	Excellent	4,800
0.2	2	—	1,000	—	—
33.0	2	7,500	750	Good	—
17.6	1	2,980	500-1,000	90%	6,300
16.0	1	3,000	900	Good	—

*Questionnaire Data

**This device is a true flare and, as such, residence time is not a measurable parameter.

of well designed afterburners by noting the outlet temperature and residence time. Furthermore, afterburners do not possess the inherent limitations to which scrubbers are subject. Any combustible material can be incinerated if the temperature and residence time are sufficiently high. The temperatures and residence times reported are usually consistent, in a general way at least, with the efficiencies reported.Beyond that, it is not possible to either affirm or deny the reported performance.

Similar comments apply to the questionnaire returns on catalytic afterburners. Again, if the temperature is high enough (up to the point at which the catalyst is damaged), enough catalyst is used and the catalyst is maintained properly, most materials can be oxidized efficiently. The efficiencies reported ("good" to "excellent", or 90% to 95%) are at least feasible in the light of the operating conditions reported. Since no information is given on catalyst maintenance or replacement, it is not possible to determine which, if any, of the respondents is optimistic in his reports.

3. Fabric Filters — Fabric filters, usually bag type filters, were the most commonly employed pollution control device reported in the questionnaires. Tables 52, 56 and 57 summarize the questionnaire results obtained. They are used for control of dry particulate from loading, mills, etc. Bag filters are known to attain very high efficiencies (99%+) even on sub-micron particulate in a properly designed system. Where reported, efficiencies usually were given as 90% or better. Since the normal application of fabric filters in the paint industry is for clean, dry particulate at ambient temperatures, there is no reason to doubt that very high efficiencies can be obtained.

Some additional source test data other than that contained in the questionnaires has been collected from other plants and source test groups. This data is presented on Table 58.

The Environmental Protection Agency retained a subcontractor to perform tests to determine the efficiency of thermal afterburners. The test methods were discussed earlier in Chapter 3. The results of their testing is presented in Table 59.

B. Operating Life and Maintenance Experience for Control Systems

This subject was not well covered by the respondents to the study's questionnaire and the results presented in Table 60 are based on data supplied from other sources. The Normal Life listed are based on trouble-free operation and do not consider the past losses caused by explosions and fires.

In general maintenance is not a significant operating cost. Cost for thermal afterburners with heat exchangers will run higher than those without. This is caused by tube fouling, tube burnout and metal failure due to thermal expansion inherent with the use of metal exchangers. Good design will keep these maintenance costs to a minimum.

TABLE 56*

TYPE 2 PLANTS

AIR POLLUTION CONTROL — LOADING, MILLS, ETC.

FABRIC FILTERS

Paint Production MM gal/yr	Number of Devices	Total Gas Flow, SCFM	Air to Cloth Ratio
1.7	1	5,000	2.5
2.4	11	7,000	2.0
0.5	1	—	—
0.7	1	5,000	6.3
1.1	2	3,850	4.0
2.5	3	10,500	2.9
0.8	1	—	—
1.2	1	—	—
0.5	1	2,000	25.0
0.2	1	83	25.5
0.2	2	1,231	8.2
6.0	3	—	—
0.1	1	—	—
1.8	1	5,600	7.0
0.6	1	—	—
0.7	1	—	—
2.5	1	2,376	2.0
1.3	1	2,700	9.0
0.1	1	875	41.7
0.7	1	1,231	8.2
0.6	1	—	—

*Questionnaire Data

TABLE 56 (Continued)

Paint Production MM gal/yr	Number of Devices	Total Gas Flow, SCFM	Air to Cloth Ratio
2.4	1	1,200	8.0
2.7	1	200	1.8
0.8	2	924	3.5
0.1	1	—	—
2.4	4	11,500	—
1.3	1	2,100	—
0.6	2	2,788	—
0.6	2	5,600	20.9
1.2	1	1,200	10.7
1.2	3	18,000	—

TABLE 57*

TYPE 3 PLANTS

AIR POLLUTION CONTROL — LOADING, MILLS, ETC.

FABRIC FILTERS

Resin Production, MM pounds/yr	38.0	80.0
Number of Devices	1	3
Total Gas Flow, SCFM	1,900	12,000
Air to Cloth Ratio	2.8	3.9

MECHANICAL

Resin Production, MM pounds/yr	2.6	80.0
Number of Devices	4	4
Total Gas Flow, SCFM	11,000	—
% Efficiency	90	—

*Questionnaire Data

TABLE 58*

TEST RESULT OF CONTROL EQUIPMENT EFFICIENCIES

Location	Type	Emission type	Operating temperature °F	Inlet ppm C_1	Outlet ppm C_1	Conversion %
Oakland, California	Thermal	Resin kettle	1300°F	6,854	206	91%
Pennsauken, New Jersey	Thermal	Solvent fumes	–	620	51	92%
				1,220	59	95%
Cincinnati, Ohio	Thermal	Open and closed kettles	1300°F	424	32	93
				1,158	37	97
			1400°F	651	15	97.7
				765	14	98.2
Withheld	Water cooled condenser	Polyester fusion cook	10 SCFM	120% LEL	80%	33%
Withheld	Double venturi water ejector	Polyester fusion cook	735 SCFM	130% LEL	122% LEL	6.5%
Commerce, California	Recirculating water scrubber	Polyester reactor	60 SCFM/25 gph	200% LEL	160% LEL	20% clear stack
			80 SCFM/25 gph	200% LEL	180% LEL	10% visible stack

*Questionnaire Data

TABLE 59

THERMAL AFTERBURNER TEST DATA

Kettles Operating During Test Period:

1. 1,000 Gallon Alkyd
2. 1,250 Gallon Polyester
3. 2,900 Gallon Latex Emulsion

Afterburner Operating Conditions:

1. 1,500°F
2. 0.5 Seconds Residence Time
3. 2,000 SCFM Total Flow

Summary*

Time (Hr)	Inlet, lb/hr THC	NO	NO_x	CH_4	Outlet, lb/hr THC	NO	NO_x	CH_4	% Efficiency (Non-Methane)
0.5	9.02	—	0.0075	0.0303	1.08	0.0493	0.301	0.293	91
1.75	6.69	0.0038	0.0058	—	0.96	0.0557	0.287	0.122	87
3.0	8.46	0.0021	0.0036	0.0219	0.92	0.0492	0.314	0.306	93
4.0	10.9	0.0055	0.0095	0.0186	1.06	—	—	0.418	94
5.25	8.54	0.0036	0.0056	0.0052	1.12	0.0442	0.316	0.487	93
6.25	8.02	0.0025	0.0039	0.0104	0.99	—	—	0.424	93
8.5	10.3	0.0034	0.0052	0.0052	1.17	0.0562	0.335	0.388	92

*The complete set of data is presented in Appendix D on Table D-17. Only those points for which both inlet and outlet methane concentrations are given are included in this summary.

TABLE 60

OPERATING LIFE AND MAINTENANCE REQUIREMENT FOR AIR POLLUTION CONTROL EQUIPMENT

TYPE	NORMAL LIFE YEARS	— MAINTENANCE EXPERIENCE — AMOUNT	ANNUAL COST*
SCRUBBERS			
Carbon Steel	5	High	10%
Stainless Steel	10	Medium	5%
THERMAL AFTERBURNERS			
Without Heat Exchanger	15	Medium	2%
With Heat Exchanger	10	Medium	3.5%
CATALYTIC AFTERBURNERS			
Unit Only With & Without Heat Exchanger	15	Low	2%
Catalysts Only	3	High	10%
FABRIC FILTERS			
Unit Only	20	Low	2%
Bags Only	2 to 4	Medium	10%

*Percent of initial equipment cost—does not include replacement cost.

For catalytic afterburners the maintenance cost for units with or without heat exchangers are about the same. This is true since these units operate at much lower temperatures and in either case are built of all metal construction.

Maintenance costs for scrubbers are primarily dependent on the degree of corrosion experienced. This is primarily a function of the acidity of the scrubbing liquid which will vary significantly with the amount of fresh water used. Scrubbers utilizing once-through water will have a longer life than that listed on Table 60.

V. CAPABILITY TO MEET MORE STRINGENT STANDARDS

A. Fabric Filters

Removal of pigment and other dry particulate is accomplished by use of fabric filters. As discussed earlier, this control device is capable of efficiencies approaching 99.9 and should have no difficulty meeting more stringent standards.

B. Afterburners

Either catalytic or thermal afterburners can be operated at increased efficiencies to meet more stringent air pollution control standards. For thermal afterburners this can be accomplished by increased operating temperature assuming additional fuel is available. For reactions that are time limited, efficiencies can be increased by increasing the residence time. This can be accomplished by reducing gas flow or adding length to the existing unit.

The efficiency of catalytic afterburners can also be increased by increasing the operating temperature and/or increasing the amount of catalyst used. To maintain higher efficiency it will probably also be necessary to shorten the catalyst maintenance cycle and the reactivation or replacement period.

C. Scrubbers

There is little that can be done to improve the efficiencies of the type of scrubbers that are currently used in this industry. They are fairly effective for removal of large particulate and heavy condensibles. They are very ineffective on noncondensible organic materials and small particulate. Changes in operating conditions that would normally improve scrubber efficiency (i.e. pressure drop, gas to liquid ratio) should have little effect on these emissions. This is typical of scrubber operation on emissions which have a wide size range of particulate. The large material is easily collected with any type of scrubber while small particulate and gaseous emission require a special scrubber operated at very high pressure drops.

D. Refrigerated Condensers

There has been only limited experience in the operation of this device. It appears that its average maximum efficiency will run around 90%. The possibility of this device meeting high efficiency standards that might develop in the future is remote.

VI. WATER AND SOLID WASTE PROBLEMS ASSOCIATED WITH BEST CONTROL

One of the many advantages of the use of afterburners for best control is the elimination of all water and solid waste problems associated with other control methods. In fact, in many cases the liquid waste solvent discussed earlier in Section III B-6 can be used as a fuel for the afterburner. This not only solves a waste disposal problem but also reduces afterburner operating cost.

The pigment dust collected in fabric filters presents no serious solid waste disposal problem. The quantities are small, non-hazardous, and may be disposed of by scavenger services in land fill operations. In many cases, they are also recycled back into paint production for use in such items as dark primers.

CHAPTER 6

INSPECTION PROCEDURES

This section is written for a compliance inspector who is familiar with inspection procedures and testing procedures in general. The best single source of background information for the compliance inspector is the Field Operations and Enforcement Manuals for Air Pollution Control, Volume I, Organization and Basic Procedures — APTD-1100, and Volume II, Control Technology and General Source Inspection — APTD-1101. These two volumes are published by the Federal Environmental Protection Agency and may be obtained from the National Technical Information Center, Springfield, Virginia 22151. The purpose of this chapter will be to detail the particular emission problems and control techniques specific to the paint and varnish industry and to help enforcement officers when entering and inspecting these facilities.

I. NATURE OF SOURCE PROBLEMS

The paint and varnish industry is one of the more complex of the chemical industries. The three basic manufacturing operations in this industry are varnish cooking, resin cooking and paint blending. The air pollution regulations most often applied to this industry are the nuisance regulations covering odor and visible emissions. The other significant problem of this industry is the emission of fugitive solvent vapors which as yet is not covered by law in most states.

The quantity of emissions released from varnish cooking are small but still present a significant local air pollution problem because of the wide variety of highly odorous substances. The amount of varnish cooking carried out by the industry has been steadily declining and is expected to continue to decline in the future. This is especially true of the small open kettle batch which represents the more difficult to control emissions.

Resin manufacturing emissions tend to be highly cyclical in nature and consist of solvent vapors, phthalic (or other acid) anhydride, polyols (either solid or liquid) and a variety of partial reaction products. The last category is usually present in the smallest quantities but may represent the most noxious component from an odor standpoint.

Exhaust volumes for a given kettle can peak at up to 100 to 200 SCFM for short periods of time and may be essentially zero during other portions of the cook. Concentration can vary from zero up to several hundred thousand ppm.

Every cooking formula will exhibit its own particular emission characteristics. The greatest quantity of emission occurs from the paint manufacturers operation and consists primarily of solvent vapors and pigment particles. They are usually fugitive in nature and exit to the atmosphere through the general building ventilation. Their concentrations are usually quite low (<50 ppm) but the overall quantity is high due to the large quantity of ventilation air. Future OSHA and air pollution regulations will probably require the capture of these emissions at their source. This should result in low volume higher concentration emissions which can be more easily controlled.

II. PROCESS DESCRIPTION

The process narratives that follow will be specific to oil based paints and varnishes. The manufacture of water based paints is of minor importance from an air pollution point of view. This is also true of the manufacture of the resins used in the blending of water based paints since they are normally provided outside this industry in chemical process plants.

A. Paint Manufacturing

Starting with all purchased raw material, the manufacturing process for pigmented products is deceptively simple from a process viewpoint. Basically it consists of mixing or dispersing pigment and vehicle to give the final product. This is schematically illustrated in Figure 57.

The paint vehicle is defined as the liquid portion of the paint and consists of volatile solvent and non-volatile binder such as oils and resins. The non-volatile portion is also called the vehicle solid or film former. The pigment portion of the paint consists of hiding pigments such as titanium dioxide (TiO_2), extenders or fillers such as talc or barium sulfate, and any mineral matter used for flatting or other purposes.

The incorporation of the pigment in the paint vehicle is accomplished by a combination of grinding and dispersion or dispersion alone. When it is necessary to further grind the raw pigment, the pebble or steel ball mills are normally used. With the advent of fine particle grades of pigment and extenders, as well as the widespread use of wetting agents, the trend is toward milling methods that are based on dispersion without grinding. This dispersion consists of breakup of the pigment clusters and agglomerates, followed by wetting of the individual particles with the binder or vehicle. Some of the more popular methods currently being used are high speed disc impellers, high speed impingement mills and the sand mill.

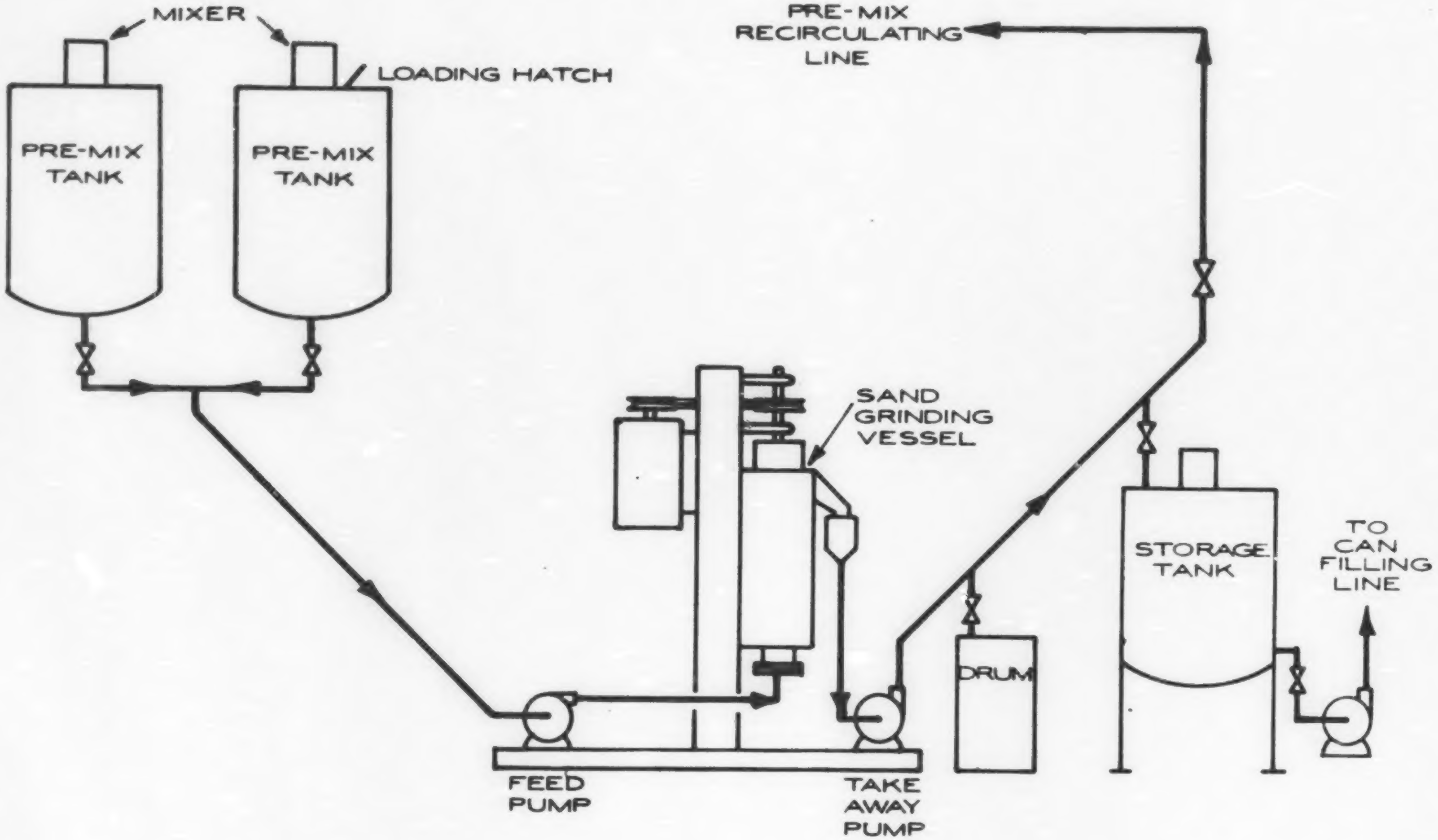


FIGURE 57

PAINT MANUFACTURING USING
SAND MILL FOR GRINDING OPERATION

Aside from this dispersion step, pigment paint manufacturing involves handling of raw material as well as handling and packaging of finished product. Operations of a typical plant may be summarized as a raw material and finished product handling problem with a variety of interdispersed batch operations. The interrelationship of all these operations is schematically illustrated in Figure 58. The operations depicted are those of a plant that makes its own resins and produces both trade sale and industrial finishes.

Some of the larger and a few of the medium size manufacturers produce a significant amount of their formulation ingredients, including pigments, resins and modified oils. Certain manufacturers produce these ingredients in an amount exceeding their requirements and sell the excess to other manufacturers. A significant number also produce only a portion of their resins and purchase the remainder from their competitors or suppliers who specialize in resin manufacturing.

B. Varnish Cooking

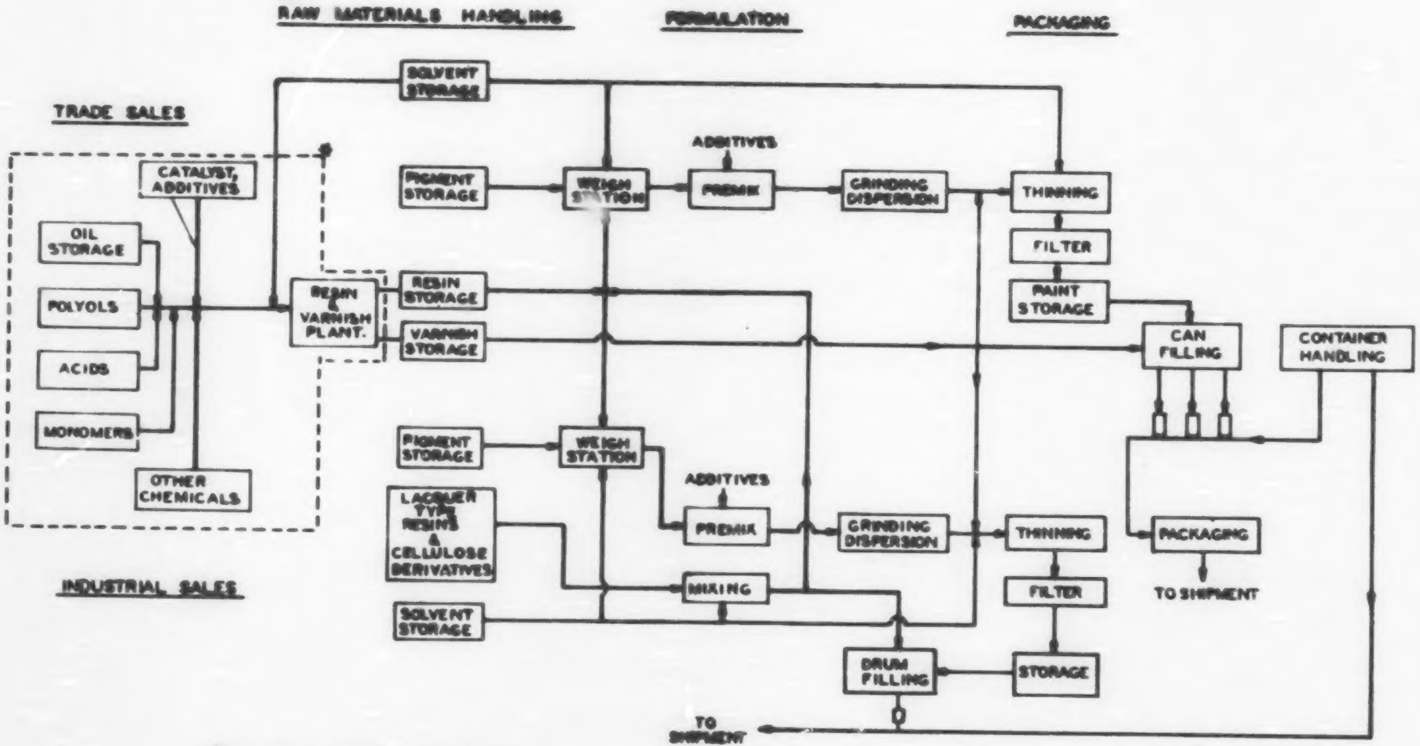
The manufacturing of resins and varnishes is by far the most complex process in a paint plant, primarily as the result of the large variety of different raw materials, products and cooking formulas utilized. The complexity begins with the nomenclature used in classification of the final product. Originally, varnishes were all made from naturally occurring material and they were easily defined as a homogeneous solution of drying oils and resins in organic solvents. As new synthetic resins were developed, the resulting binders or varnishes were classified on the basis of the resins used. Examples of this are alkyd, epoxy and polyurethane resin varnishes.

There are two basic types of varnishes, spirit varnishes and oleoresinous varnishes. Spirit varnishes are formed by dissolving a resin in a solvent. They dry by solvent evaporation. Shellac is a good example of a spirit varnish. Another material that might fall in this category is lacquer. Technically, lacquers are defined as a colloidal dispersion or solution of nitro-cellulose, or of similar film-forming compounds, with resins and plasticizers, in solvent and diluents which dry primarily by solvent evaporation. Oleoresinous varnishes, as the name implies, are solutions of both oils and resins. These varnishes dry by solvent evaporation and by reaction of the non-volatile liquid portion with oxygen in the air to form a solid film. They are classified as oxygen convertible varnishes and the film formed on drying is insoluble in the original solvent. A summary of the various types of material used in the production of classical varnishes is given in Table 61.

Varnish is cooked in both portable kettles and large reactors. Kettles are used only to a limited extent and primarily by the smaller manufacturers. The very old, coke fired, 30 gallon capacity copper kettles are no longer used. The varnish kettles which are used, have capacities of 150 to

FIGURE 30

MATERIALS FLOW SHEET FOR PAINT MANUFACTURING



* MANY PLANTS PURCHASE
RATHER THAN MANUFACTURE
THEIR RESINS AND VARNISHES

TABLE 61

VARNISH RAW MATERIALS[2]

Oils	Resins	Solvents	Driers	Additives
1. Hard	1. Natural	1. Mineral Spirits	1. Lead	1. Anti-Skinning agents
a. Tung	a. Fossil resin, congo kauri, pontianak	2. VM&P Naphtha	2. Manganese	2. Ultra-violet absorber
b. Oiticica	b. Semi-fossil resin manila, boea, batu, eastindia	3. Toluol	3. Cobalt	3. Flattening agents
c. Dehydrated castor oil	c. Recent and crop resin dammar, accroides sandaral mastic, elemi, shellac	4. Xylol	4. Calcium	
2. Soft	d. Rosin, gum rosin, wood rosin, tall oil rosin, rosin esters	5. Terpene solvents	5. Zirconium	
a. Linseed	2. Synthetic Resin			
b. Safflower	a. Maleic resin, phenolic resin			
c. Soya	3. Metallic Soaps			
d. Fish	a. Limed rosin			
e. Tall oil fatty acids	b. Zinc resinate			
3. Chemically modified				
a. Maleic-treatment				

375 gallons. These are fabricated of stainless steel, have straight sides and are equipped with three or four-wheel trucks. Heating is done with natural gas or fuel oil for better temperature control. The kettles are fitted with retractable hoods and exhaust pipes, some of which may incorporate solvent condensers. Cooling and thinning are normally done in special rooms. A typical varnish production operation is illustrated in Figure 59.

The manufacturing of oleoresinous varnishes is somewhat more complex than for spirit varnishes. This manufacture consists of the heating or cooking oil and resins together for the purpose of obtaining compatability of resin and oil and solubility of the mixture in solvent, as well as for development of higher molecular weight molecules or polymers.

The time and temperature of the cook are the operating variables used to develop the desired end product polymerization or "body". The chemical reactions which occur are not well defined. The resin is a polymer before cooking and may or may not increase in molecular size during the cook. This resin may react with the oil to produce copolymers of oil and resin or it may exist as a homogeneous mixture or solution of oil homopolymers and resin homopolymers.

It is possible to blend resins and heat-bodied oil and obtain the same varnish that can be produced by cooking the resin and the unbodied oils. This indicates that copolymerization is not the fundamental reaction in varnish cooking.

Heat bodying or polymerization of an oil is done to increase its viscosity and is carried out in a kettle in a fashion similar to varnish cooking. The fundamental reaction that occurs is polymerization of the oil monomers to form dimers with a small portion of trimers.

C. Resin Manufacturing

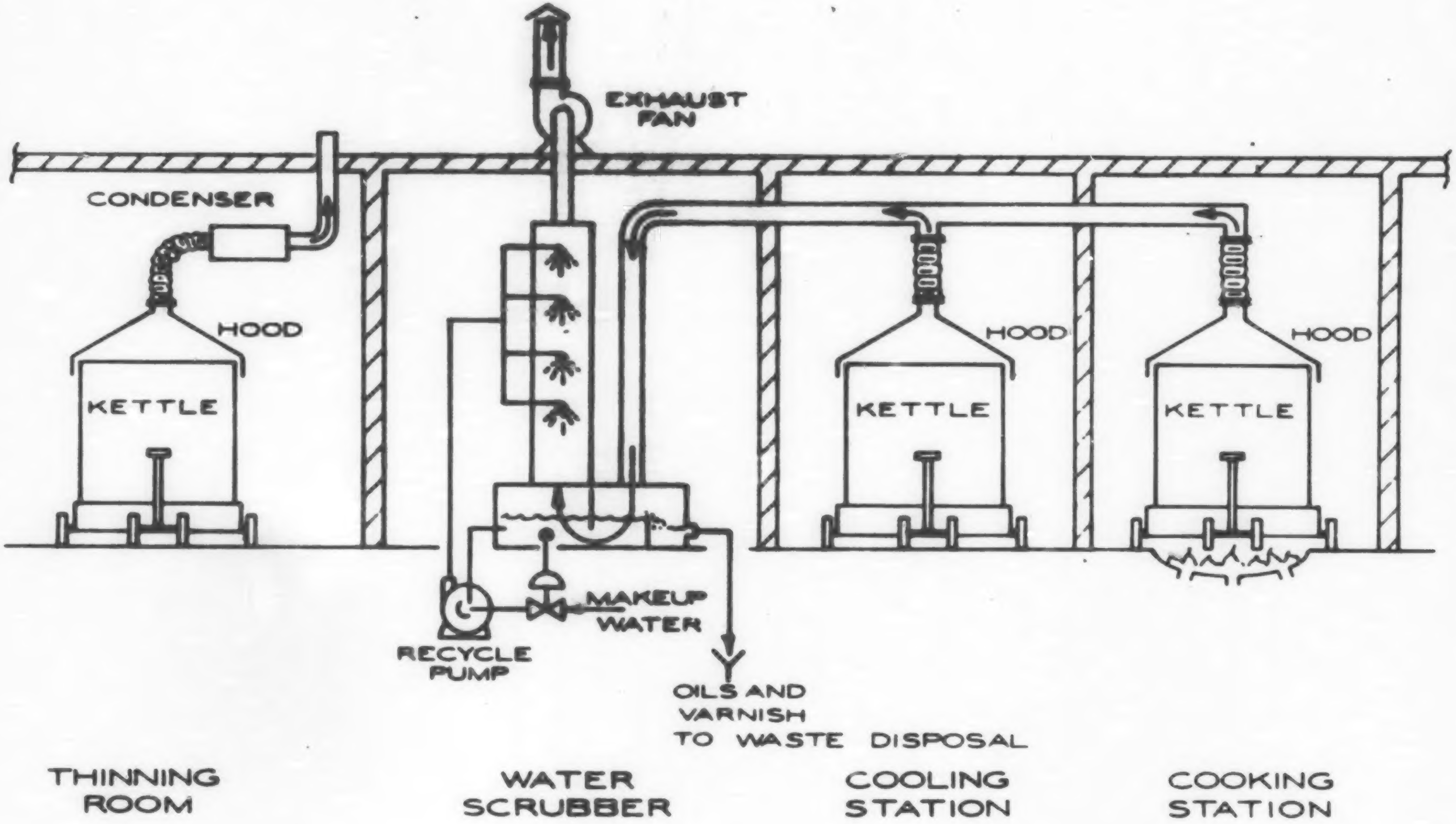
There is a large variety of synthetic resins produced for use in the manufacture of surface coatings. A listing of the more popular resins is given below. They are listed by order of consumption by the coatings industry:[3]

Alkyd
Vinyl
Acrylic
Epoxy
Cellulosic
Amino
Urethane
Rosin Ester
Styrene Butadiene
Phenolic
Hydrocarbon

By far the most widely used of these resins are the alkyds and the vinyls. Alkyd consumption is approximately twice that of the vinyl. Further discussion will concentrate on alkyd resins.

FIGURE 59

TYPICAL VARNISH COOKING ROOM



Alkyd resins comprise a group of synthetic resins which can be described as oil-modified polyester resins. They are produced from the reaction of polyols or polyhydric alcohol, polybasic acid and oil or fatty monobasic acid. A listing and discussion of commonly used raw materials will follow.[2]

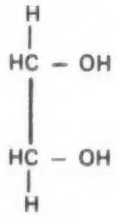
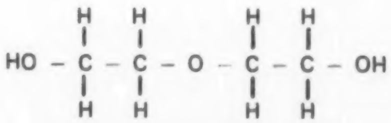
1. Oils or fatty acid

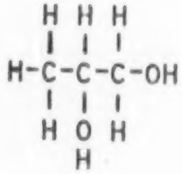
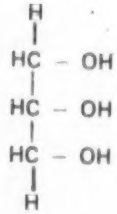
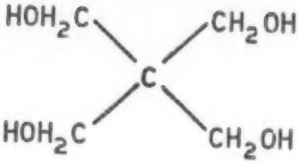
Linseed
Soybean
Safflower
Tall Oil Fatty Acid
Tall Oil
Fish
Tung (minor)
Oiticica (minor)
Dehydrated Castor (minor)

Castor
Coconut
Cottonseed
Lauric Acid
Pelargonic Acid
Isodecanoic Acid

The materials in the first column are oxidizing or drying types. The materials in the second column are non-oxidizing and yield soft non-drying alkyds which are used primarily as plasticizers for hard resins. The acids shown in this column are the only materials that are strictly synthetic in origin.

2. Polyols

Name	Formula	Form
Ethylene glycol	 $\mathrm{HOCH_2{-}CH_2OH}$	Liquid
Diethylene glycol	 $\mathrm{HO{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}OH}$	Liquid

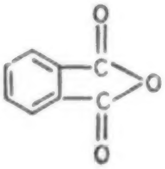
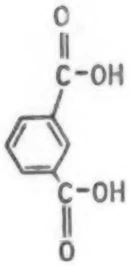
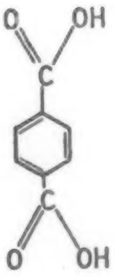
Propylene glycol		Liquid
Glycerine CP-95% glycerine Super-98%		Liquid
Pentaerythritol		White Solid

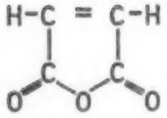
Glycerol or glycerine was the first polyol used for alkyds and is still widely used.

The first polyol, based on usage, is pentaerythritol (PE), which came into common use in the 1940's. PE is supplied as "technical grade" material and contains mono, di, tri and polypentaerythritol. The material consists primarily of the mono form which was illustrated previously in the list of polyols.

The important distinguishing feature of the various polyols is the number of potentially reactive hydroxyl groups in the molecule, known as functionality. The glycols with a functionality of two produce only straight chain polymers and their resins are soft and flexible. The resultant products are used primarily as plasticizers for hard resins. Glycerine has a functionality of three and is used primarily in short and medium oil alkyds. Pentaerythritol, with a functionality of four, cross-links to a greater extent, forming harder polymers. It is ideal for use in long oil alkyds.

3. Acids and Anhydrides

Name	Formula	Form
Phthalic anhydride (ortho)		White Solid
Isophthalic acid (meta)		White Needles
Terephthalic acid (para)		White Crystals

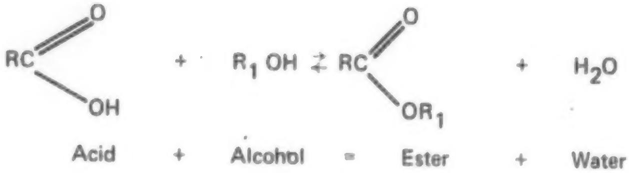
Maleic anhydride		White Solid

The acidic material can be used as an acid or anhydride. The anhydride is formed from two molecules of acid minus a molecule of water or removal of one molecule of water from a diacid. It is preferred, since it reacts faster and yields less water for removal from the cook.

For many years, phthalic anhydride (ortho) (PA) was the only polybasic acid used in substantial proportions in alkyds. It still remains the predominant dibasic acid. PA is produced from the catalytic oxidation of naphthalene or ortho-xylene.

The chemistry of alkyd resin systems is very complex. So much so that theoretical considerations offer only a good starting point. Final formula and variations are developed by trial and error changes, based on performance requirements and shortcomings of previous batches.

Condensation is the reaction basic to all polyester resins, including alkyds. This reaction follows the elementary equation for esterification as shown below:



For Alkyd Resins

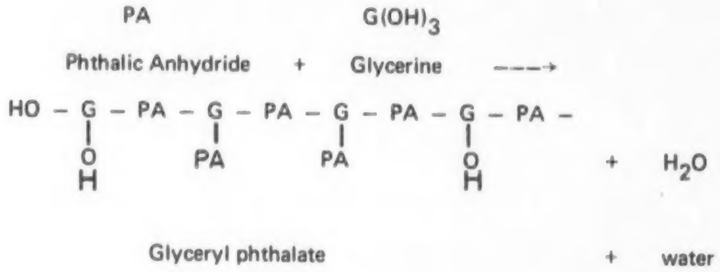
$$PA + Glycerine \rightleftharpoons Ester + H_2O$$

The ester monomer formed is very complex and further reacts to form large polymers called resins. The polymers formed are low in molecular weight by comparison to other resins. For example alkyd resins have molecular weights ranging from 1,000 to 7,000 while some vinyl and acrylic resins have average molecular weights in excess of 100,000 and in some cases as high as 500,000.

The alkyd polymers also react with oil or fatty acid and are generally classified by the amount of oil or PA used in the formulation, as described below:

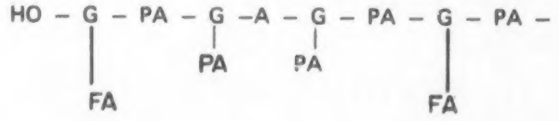
	% Oil	% PA
Short Oil	33 to 45	35
Medium Oil	46 to 55	30 to 35
Long Oil	56 to 70	20 to 30
Very Long Oil	71 up	20

The resulting reactants of the PA, polyol and oil may be represented in part as shown below:



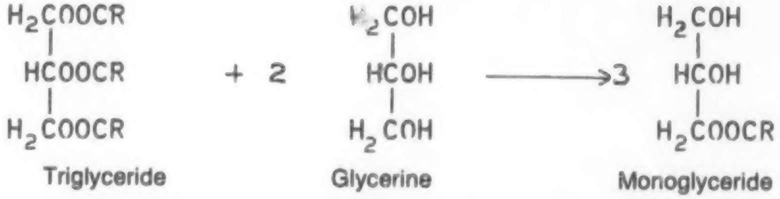
$$\underset{\text{Phthalic Anhydride}}{\mathrm{PA}} + \underset{\text{Glycerine}}{\mathrm{G(OH)_3}} \dashrightarrow \underset{\text{Glyceryl phthalate}}{\mathrm{HO-\underset{\underset{H}{O}}{G}-PA-\underset{PA}{G}-PA-\underset{PA}{G}-PA-\underset{\underset{H}{O}}{G}-PA-}} + \underset{\text{water}}{\mathrm{H_2O}}$$

This will then react with the long chain oil monoglyceride or fatty acid (FA) to yield:



$$\mathrm{HO-\underset{FA}{G}-PA-\underset{PA}{G}-A-\underset{PA}{G}-PA-\underset{FA}{G}-PA-}$$

Alkyds can be manufactured directly from a fatty acid, polyol and acid or from oil, polyol and acid. The second combination (oil, glycerine and PA) produces glyceryl phthalate which is insoluble in the oil and precipitates. This problem can be overcome by first converting the oil to a monoglyceride by heating with a polyol in the presence of a catalyst. This process is called alcoholysis of the oil. The basic reaction is shown below:



$$\underset{\text{Triglyceride}}{\begin{matrix}\mathrm{H_2COOCR}\\|\\\mathrm{HCOOCR}\\|\\\mathrm{H_2COOCR}\end{matrix}} + 2\ \underset{\text{Glycerine}}{\begin{matrix}\mathrm{H_2COH}\\|\\\mathrm{HCOH}\\|\\\mathrm{H_2COH}\end{matrix}} \longrightarrow 3\ \underset{\text{Monoglyceride}}{\begin{matrix}\mathrm{H_2COH}\\|\\\mathrm{HCOH}\\|\\\mathrm{H_2COOCR}\end{matrix}}$$

This is an ester interchange reaction with no loss of water.

When fatty acid rather than oil is used as the starting material, this is called the "one-stage" process. In this process, the fatty acid and glycerine are added to the kettle, the agitator is started and heat is introduced. When the batch reaches 440°F, the PA is slowly added and cooking continued for another 3 to 4 hours until the desired body and acid number are reached.

If the fusion process is being used, a continuous purge of inert gas is maintained to remove the water formed in the reaction. This water may also be removed by what is known as the solvent process. It is similar to the fusion process except that about 10% aromatic solvent (usually xylene) is added to the start. The vaporized solvent is passed into a condenser. The condensate then flows to a decant receiver for separation of reaction water. Recovered solvent is returned to the reactor. Inert gas flow in solvent cooking is very low and in some cases is not used.

As discussed earlier, when oil is used rather than fatty acid, the alkyds are produced in a two-stage process. In the first stage the monoglyceride is first produced from the linseed oil and glycerol. Catalyst and oil are added and the alcoholysis of the polyol and oil is carried out between 450 and 500°F until the desired end point is reached. When the alcoholysis is completed, any additional polyol needed is added.

Following this, the required amount of PA and esterification catalyst are slowly added. If solvent cooking is to be used, the solvent is also added at this time. Cooking then proceeds as before.

A typical manufacturing formula for a 50% oil-modified glyceryl phthalate alkyd using the two-stage process is given below.

	lb
First stage	
Linseed oil	51.3
Glycerol (95%)	12.8
Catalyst, $Ca(OH)_2$	0.026
Second stage	
Glycerol (95%)	6.2
Phthalic Anhydride	39.7
Catalyst	
Methyl p-Toluene Sulfonate	0.2
	110.2
Approx. Loss	10.2
Solids Yield	100.0

Alkyd and other resins are cooked in closed kettles, more properly called reactors. They vary in size in commercial production from 500 to 10,000 gallons. A typical reactor system is shown in Figure 60. They are generally fabricated of Type 304 or 316 stainless steel with well polished surfaces to assure easy cleaning. Design pressure is usually 50 psig. These reactors may be heated electrically, direct fired with gas or oil, or indirectly heated using a heat transfer media such as Dowtherm®. They are also equipped with a manway, sight-glass, charging and sampling line, condenser system, weigh tanks, temperature measuring devices and agitator. The manway is used both for charging solid material and for access to the kettle for cleaning and repair.

The reactor may be equipped with a variety of different condenser systems. The system shown in Figure 60 includes a packed fractionating column, a reflux condenser and a main condenser. The condensers are water cooled shell and tube type and may be either horizontally or vertically inclined. Vapors are processed and condensed on the tube side and drain to a decant receiver for separation and possible return of solvent to the reactor. A dual function aspirator venturi scrubber is often added to the system. It is used to ventilate the kettle during addition of solid materials and may also remove entrained unreacted or vaporized solids and liquids from the venting gases.

Thinning tanks are always included as part of the reactor system. They are normally water cooled and equipped with a condenser and agitator. The partially cooled finished alkyd is transferred from the reactor to the partially filled thinning tank. Since most alkyd resins are thinned to 50% solids, the capacities of these tanks are normally twice the capacity of the reactors. These tanks are also frequently mounted on scales so that thinning solvents may be accurately added.

The final step in a reactor system is filtering of the thinned resin prior to final storage. This is normally done while it is still hot. Filter presses are the most commonly used filtering device.

The manufacturing procedures and equipment used for the production of other resins listed at the beginning of this discussion are quite similar. The major differences are the raw materials and the process steps utilized. A detailed discussion of these other resins is beyond the scope of this narrative.

D. Air Pollution Control Techniques

Collection of particulate pigment or resin emission is a simple straightforward job. The only practical control device is a fabric filter, and it is ideally suited for this application. Collection efficiency for the submicron pigment dust (0.05 to 0.25 microns) is in the range of 99.9%. There are no temperature problems since the exhaust system runs at ambient temperatures. The grain loading is very low and baglife is extensive. Approximately 0.01% of the loaded pigments are lost and collected. Grain loadings to the fabric filter run around 0.19 grain/SCF. A typical collection

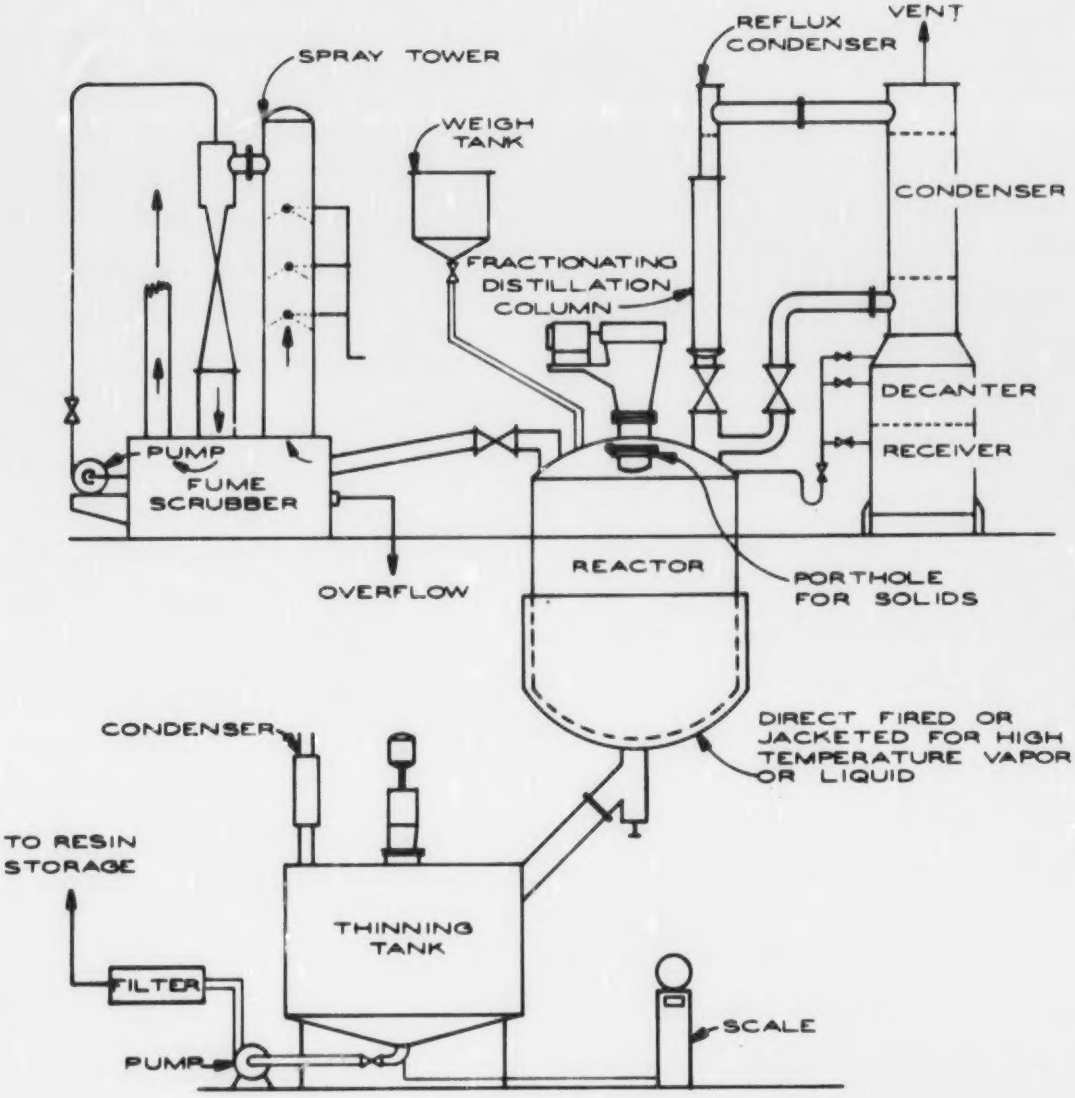


FIGURE 60
MODERN RESIN PRODUCTION SYSTEM

system is shown in Figure 61. The collection system can be a fixed hood which can handle both dust and pigment bags or a flexible hose positioned above the loading hatch or attached to the top of the tank. The tank attachment provides the most positive control of fugitive dust emission but also increases pigment and solvent losses slightly.

The application of control equipment to this problem is quite simple and can be solved with standard off-the-shelf equipment from a host of suppliers.

The control of hydrocarbon and odors from the various emission sources listed earlier is not quite as straightforward as the dust emission. There are three types of control equipment that have been applied to this problem. They are catalytic and thermal combustion devices and wet scrubbers.

As a general rule, wet scrubbing does not provide a satisfactory solution for the following reasons:

1. Removal efficiency of fine hydrocarbon aerosol is not good at economically practical pressure drops.
2. Noncondensible hydrocarbon solvent vapors will not be removed.
3. Odor removal without the addition of an oxidizing agent such as potassium permanganate or sodium hypochorite is unsatisfactory. If an oxidizing agent is used, operating cost will be quite high due to the high concentration of other oxidizable material such as phthalic anhydride, resins and oil.
4. Mobile packing and high make-up water rates are required to prevent plugging of the scrubber beds and spray nozzles.
5. Correction of the air pollution problem with wet scrubbing causes an equivalent water pollution problem.

The only control technique currently being used that has proven effective for all cases is combustion. Three general methods are employed to combust waste gases, as shown below.

1. Flame Incineration
2. Thermal Combustion
3. Catalytic Combustion

All of the above methods are oxidation processes. Ordinarily, each requires that the gaseous effluents be heated to the point where oxidation of the combustible will take place. The three methods differ basically in the temperature to which the gas stream must be heated.

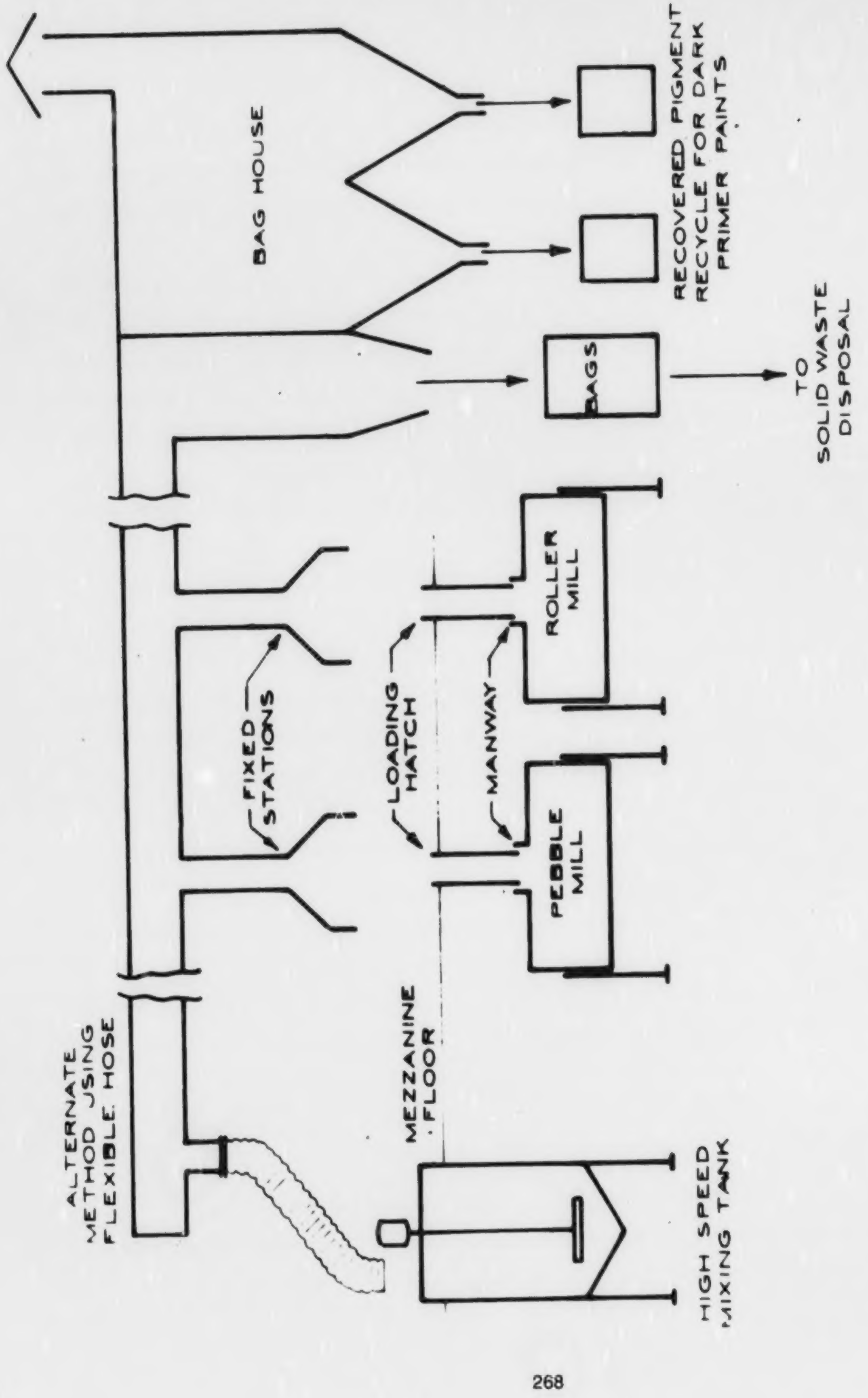


FIGURE 61
PIGMENT EMISSION CONTROL SYSTEM

Flame incineration is the easiest of the three to understand, as it comes the closest to everyday experience. When a gas stream is contaminated with combustibles at a concentration approaching the lower flammable limit, it is frequently practical to add a small amount of natural gas as an auxiliary fuel and sufficient air for combustion when necessary, and then pass the resulting mixture through a burner. The contaminants in the mixture serve as a part of the fuel. Flame incinerators of this type are most often used for closed chemical reactors. They are not used on resin reactors at present. They may be an ideal solution some day, however, when methods of operating a closed, pressurized resin reactor are developed.

It is far more likely that the concentration of combustible contaminants in an air stream will be well below the lower limit of flammability. When this is the case, direct thermal combustion is considerably more economical than flame combustion. Direct thermal combustion is carried out by equipment such as that illustrated in Figure 62. In this equipment, a gas burner is used to raise the temperature of the flowing stream sufficiently to cause a slow thermal reaction to occur in a residence chamber. Whereas flame temperatures bring about oxidation by free radical mechanisms at temperature of 2500°F and higher, thermal combustion of ordinary hydrocarbon compounds begins to take place at temperatures as low as 900 to 1000°F. Good conversion efficiencies are produced at temperatures in the order of 1400°F with a residence time of 0.3 to 0.6 seconds.

Catalytic combustion is carried out by bringing the gas stream into intimate contact with a bed of catalyst. In this system, the reaction takes place directly upon the surface of the catalyst which is usually composed of precious metals such as platinum and palladium. While thermal combustion equipment brings about oxidation at concentrations below the limits of flame combustion, catalytic combustion operated below the limits of flammability and below the normal oxidation temperatures of the contaminants. The reaction is instantaneous by comparison to thermal combustion and no residence chamber is required. Catalytic combustion is carried out by equipment such as that illustrated in Figure 63.

In general, catalytic afterburners are less expensive to operate, however, they depend directly on the performance of the catalyst for their effectiveness. It will not function properly if the catalyst becomes deactivated. Because of this, catalytic units are not inherently functional when operated at design temperature. In many areas, means for ensuring adequate performance of the catalyst on a long term basis will be required by environmental control offices.

The basis for design of either catalytic or thermal combustion is the hydrocarbon concentration of the exhaust gases handled by the afterburner. The maximum hydrocarbon level is set by most

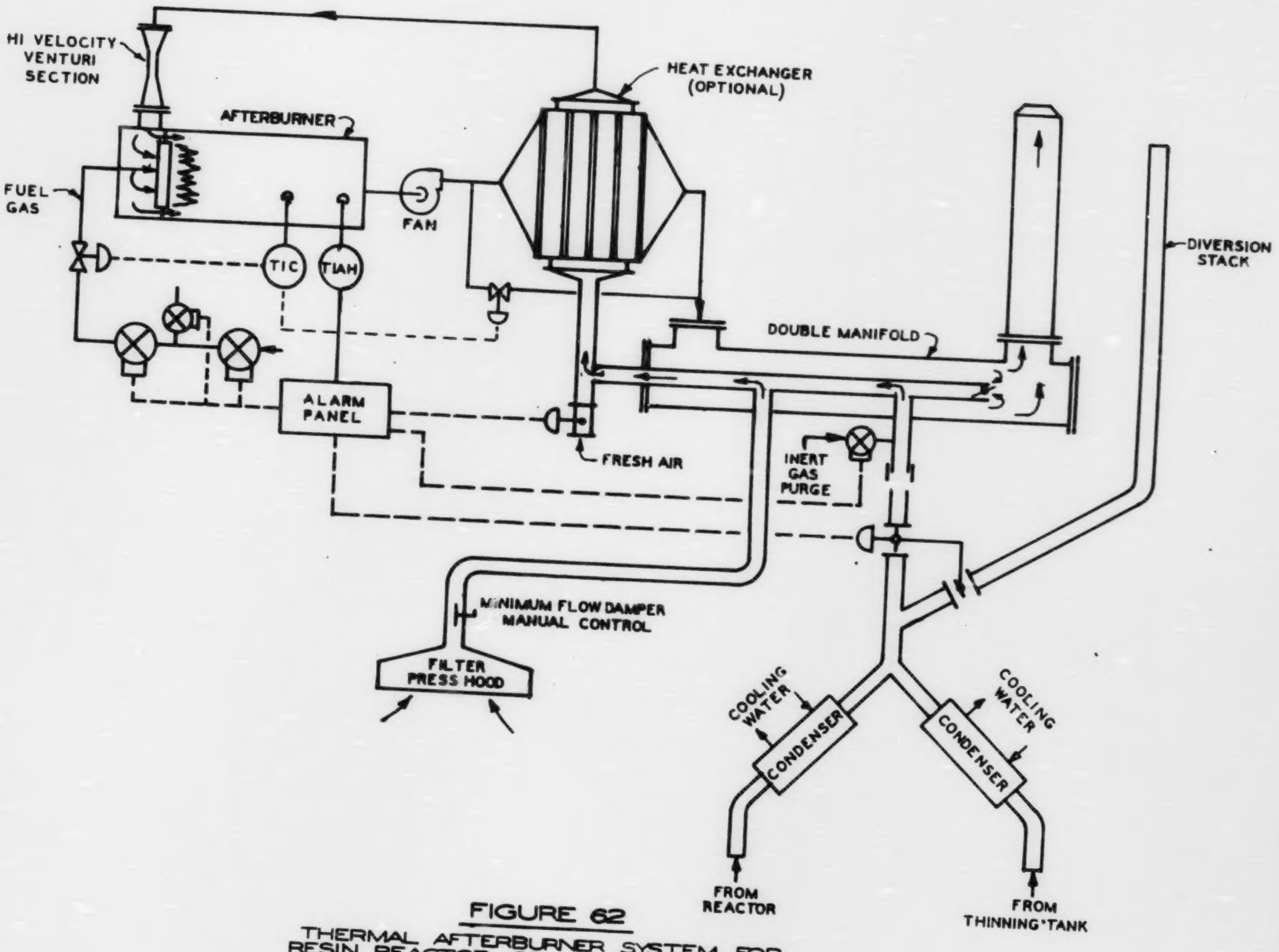


FIGURE 62

THERMAL AFTERBURNER SYSTEM FOR RESIN REACTOR OR CLOSED KETTLE

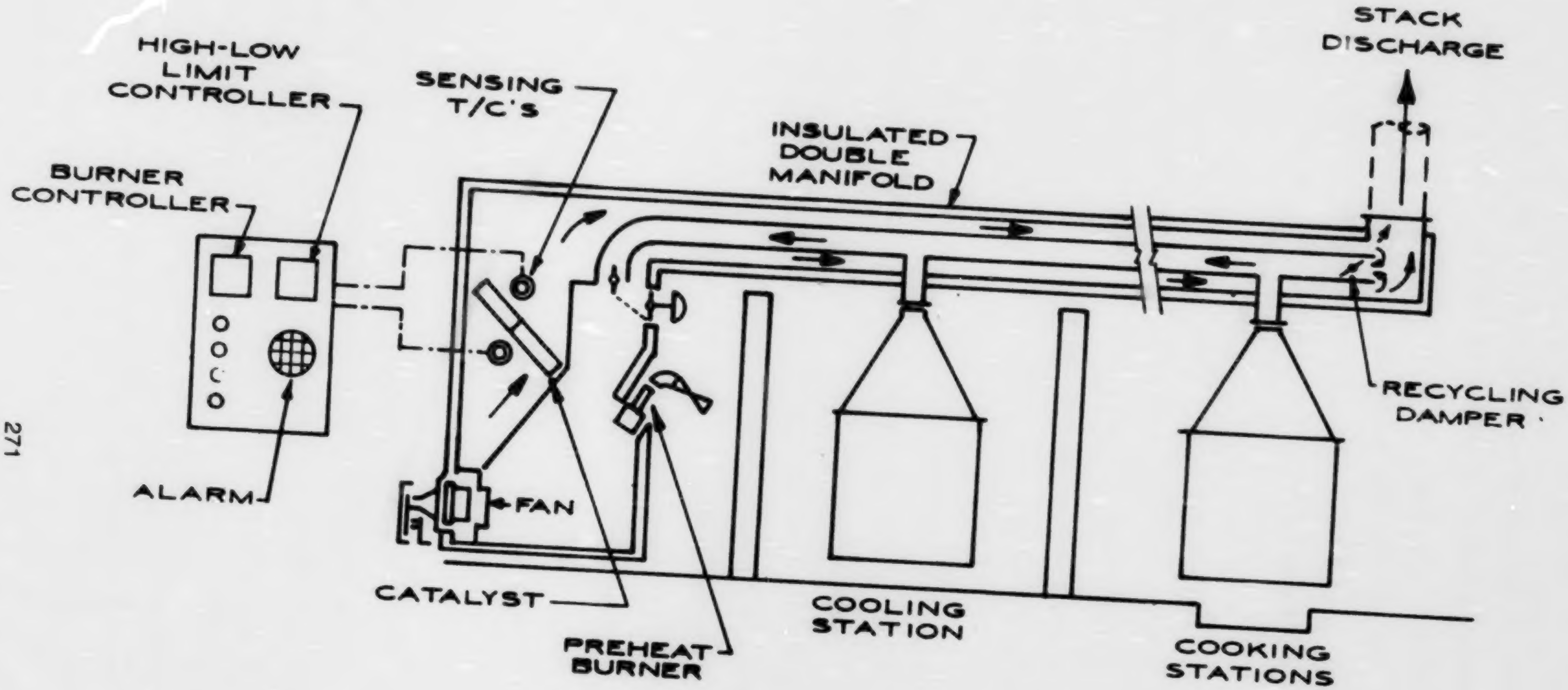


FIGURE 63
SCHEMATIC DIAGRAM OF A CATALYTIC AFTERBURNER SYSTEM FOR VARNISH KETTLES

insurance companies at one-quarter of the lower explosive limit (L.E.L.) which is equivalent to 13 Btu/SCF of exhaust gas. Once the rate of emission is determined, it is then necessary to calculate the dilution air required to meet 1/4 L.E.L. and set up the ductwork system to provide for this dilution. When possible, dilution air should be utilized to help capture as many fugitive fume emissions as possible. For example, this can be accomplished by taking the dilution air from a hood positioned over the resin filter press and venting the thinning tanks and product run-down tanks into the same system.

The major problem with catalytic or thermal afterburners as applied to open or closed resin and varnish kettles is the danger of fires and/or explosions. This has happened in numerous occasions in the past due primarily to excessive hydrocarbon emission from kettles. These problems have been all but eliminated on newer units by assuring that the design was based on actual emission measurements of the highest emitting cook and the addition of some of the following system safety features:

1. High limit temperature alarm to shut off burner and activate a diversion system.
2. High velocity duct section to assure gas flow to afterburner substantially exceeds flame propogation velocity of hydrocarbons being burned.
3. Double manifolding or hot gas recycle to prevent condensation of heavy hydrocarbons or phthalic anhydride.
4. Diversion system to block off hydrocarbon emissions to the unit, by-passing them directly out a separate exhaust, and introduction of fresh air to purge the unit.
5. Pneumatic operation of the diversion system to assure fast positive action and provide a fail-safe system in the event of either air or electrical failure.
6. Purging with inert gas in the event of power failure.

III. INSPECTION POINTS

There are few, if any, federal or state air pollution control regulations dealing specifically with the paint and varnish industry. General regulations that affect the industry are the opacity regulation and odor nuisance laws. Solvent emissions is the other area of potential problems. Most plants are quite likely to be affected by regulations such as Rule 66 of the LOS ANGELES COUNTY AIR POLLUTION CONTROL DISTRICT or Regulation 3 of the SAN FRANCISCO BAY AREA AIR POLLUTION CONTROL DISTRICT.

In preparing for an inspection of a paint and varnish plant, the air pollution inspector should be familiar with:

1. The conduct of an odor survey
2. Opacity observation
3. Classification of photochemically reactive solvents

His main task during the inspection will be:

1. Determination of visible plumes and boundary line odor levels
2. Review of process flow sheet
3. Inspection of production facilities
4. Determination of source testing requirements

Determination of compliance of the odor nuisance regulation is difficult. Consistant previous odor complaints are a good indication that a plant may be out of compliance in this area. If possible, the inspection should be arranged when the wind is blowing toward the area from which the complaints have occurred in the past. In any event, determination of odor nuisance should be made down wind from the plant before the on-site visit, since exposure to high levels inside the plant will dull sensitivity to lower odor levels. A listing of odor thresholds for material likely to be used by a paint and varnish plant was given previously in Table 28 and is presented again on the following page.

Inspection for visible stack plumes should also be made at this time. Any violation can then be further detailed during the plant inspection.

Prior to the plant inspection, an attempt should be made to meet with the plant engineer and obtain and/or develop a process flow sheet listing all potential emission points. This will aid in conducting a proper on-site inspection and a good emission inventory.

The next step is the on-site inspection of the facilities. This can be divided into the following three areas:

1. Raw material handling and storage
    a. Liquids
    b. Dry materials
2. Manufacturing
    a. Resin manufacturing
    b. Varnish cooking
    c. Paint blending
3. Filling, packaging and product storage

TABLE 28*

ODOR THRESHOLDS OF SOME ORGANIC VAPORS

Chemical	Odor threshold, ppm
Acetaldehyde	0.21
Acetone	100.0
Acrolein	0.21
Benzene	4.68
Ethanol	10.0
Ethyl acrylate	0.00047
Formaldehyde	1.0
MEK	10.0
Methanol	100.0
Methyl methacrylate	0.21
Methylene chloride	214.0
Phenol	0.0470
p-Xylene	0.47
Styrene (inhibited)	0.10
Styrene (uninhibited)	0.047
Toluene	2.14

*Air Pollution Control Assoc. Journal, Volume 19, Number 2, Feb. 1969, pages 91 to 95

A. Raw Material Handling and Storage

Liquid raw materials handled in bulk quantities will be considered first. Oils and polyols are not very volatile and can sometimes be neglected as emission sources at this point in the process. Solvents (and materials, such as resin solutions, that contain solvents) are the major potential vapor emission sources in the handling and storage stage of the plant operation. Even in this category many substances can be neglected. Many parts of the country have no regulations concerning non-photochemically reactive organics. In those localities, tanks containing such material can often be neglected if there is no apparent odor nuisance. Likewise, many localities exempt solvents having vapor pressures below some specified value. These solvents can usually be neglected on this basis. The size (capacity), contents, venting arrangement and frequency of filling of all other tanks should be noted. Particular attention should be given to the solvents known to have a high odor potential, such as isophorone, styrene, ethyl acrylate, etc.

The most important solvents that must be considered when determining compliance in most parts of the country are the relatively volatile, photochemically reactive organics. A listing of solvents commonly used in paint and varnish manufacturing is given in Table 62. Of these, the ones most often used in sufficient quantities to justify bulk storage are toluene, xylene and the lower boiling aromatic naphthas. The pumping rates for these solvents should be determined so that displacement losses can be calculated. For example, for toluene at 20°C, a pumping rate of 144 gal/min or more will give emission rates in excess of 8 pounds/hr which would violate allowable emission rates in some states. Filling losses for selected solvents is given in Table 63. Vapor pressure is strongly temperature dependent so that a solvent that can be neglected in a cold climate may have to be considered where ambient temperatures tend to be higher.

Dry materials are usually received and stored in bags or drums so they normally present no pollution potential until dumped during the manufacturing process. The same is true of liquid materials received and stored in cans and drums. Any area where mechanical transfer or handling (such as sifting, blending, etc.) of solid powders takes place in contact with air should be noted as a potential emission source.

B. Manufacturing

Attention can now be directed towards the manufacturing area. It is necessary to locate and identify all vents serving the equipment in this area. As before, in many localities, a distinction is made between photochemically reactive and non-photochemically reactive organics with the latter often exempt from the regulation. The potential for odor nuisances for non-reactive materials should

TABLE 62

CLASSIFICATION OF TYPICAL SOLVENTS

Solvents	Vapor Pressure @ 20°C (mm Hg)	Status*
Alcohols		
Methyl	97.3	exempt
Ethyl	43.9	exempt
Isopropyl	32.8	exempt
n-Butyl	4.3	exempt
sec-Butyl	12.5	exempt
Ketones		
Acetone	186.0	exempt
MEK	70.2	exempt
MIBK	15.0	not exempt
Isophorone	0.18	not exempt
Esters		
Ethyl acetate	74.4	exempt
Isopropyl acetate	43.2	exempt
n-Butyl acetate	10.0	exempt
Amyl acetate (mixed)	3.8	exempt
Ethers (and derivatives)		
Ethylene glycol monoethylether	0.1	exempt
Ethylene glycol monoethyletheracetate	2.0	exempt
Aromatics**		
Xylene	7.1	not exempt
Toluene	22.0	not exempt
Other		
2-Nitropropane	12.9	exempt
Methylene chloride	360.0	exempt
Trichloroethylene	65.0	not exempt

*These solvents are classified according to a LAAPCD Rule 66 type of definition.

**Large quantities of various mineral spirits and napthas are consumed. Some of these contain sufficient quantities of aromatics to be classified as "reactive". Each case must be considered individually, however. This is also true of vapor pressures.

TABLE 63

FILLING LOSSES FOR SELECTED SOLVENTS @ 20°C

Solvent	V.P. @ 20°C, mm	Mol. Wt.	Filling Loss, lb/100 gal
Acetone	186	58	0.494
Ethyl Acetate	74	88	0.299
Toluene	22	92	0.0927
Mineral Spirits	2 (est.)	160 (est.)	0.0147

SAMPLE CALCULATION

Material: Acetone Molar volume @ 20°C = 24 liter/g-mole

$$\text{Filling loss} = 186\text{mm} \times \frac{1}{760\text{ mm}} \times 100\text{ gal} \times 3.79\text{ liter/gal}$$

$$\times \frac{1}{24\text{ liter/g-mole}} \times 58\text{ gram/g-mole}$$

$$\times \frac{1}{454\text{ g/lb}} = 0.494\text{ lb}$$

not be overlooked. Where this is true, attention can be concentrated on those vents having photochemically reactive or odorous emissions. Regulations can change, of course, so that in the future, regulation of all organic emissions may become typical, or more refined measurements of reactivity may lead to different classifications.

The resin plant represents by far the most difficult area in which to determine compliance. The processes are so cyclic in nature and industry practice so diversified that there seems no alternative other than a continuous (or, at least, a semi-continuous) emission monitor of an entire cook. It should be noted that two vents are involved in a solvent cook and one in a fusion cook. The thin tank condenser vent and, where applicable, hood vents over the resin filter presses are other points to be considered in the resin plant. A portable anemometer capable of measuring very low velocities and a portable total hydrocarbon detector (both explosion proof) are helpful in determining compliance for these operations. Where separate standards exist for toxic materials (such as isocyanates from polyurethane production) it may be necessary to use special techniques for measuring the concentration of such materials. There is no adequate substitute for a competently conducted source test over the period of the cook to establish compliance for a resin operation.

Operations in the paint plant are relatively easier to monitor. If the only ventilation in these areas is the general building ventilation system then, in many localities, no control regulations apply. Likewise, if no reactive organic solvents or solvents with pronounced odor characteristics are used, regulations may not apply. The use of a weight balance calculation to determine emissions is not recommended in that a small difference between large numbers is usually involved. Where emissions are collected in ducts and exhausted at one or more point sources, they should be investigated for compliance. In paint plants, particulate as well as organic emissions must be considered. One system often employed in paint plants is to collect emissions (solvent vapor as well as particulate) in ductwork, pass the gas stream through a particulate collector (usually a fabric filter type) in which pigment solids are removed, and exhaust through a stack to the atmosphere. The inlet and outlet loadings for this particulate collector ordinarily need not be measured if the filter appears to be intact and the organic concentration at the stack determined. Much higher flows are encountered here than in the resin plant, and conventional source velocity and concentration measurement techniques are likely to be satisfactory.

Types of emission control devices encountered in the paint and resin industry include scrubbers, fabric filters and thermal and catalytic afterburners. The typical scrubber installation of the type usually found on resin kettles set up for fusion cooking tends to be rather ineffective on all but large particulate and heavy condensible materials. Furthermore, such scrubbers can sometimes be the source of visible plumes. Where these devices represent the only pollution control equipment in a given resin plant, some consideration might be given to source testing the plant, particularly if severe odor or visible emission problems exist.

Fabric filters probably represent the only practical reliable means of collecting pigment dust emissions applicable to most paint manufacturing facilities. Electrostatic precipitators would also be effective but so far as is known they find little if any use in the paint industry due to cost considerations. They are sometimes used in pigment manufacturing but in that case their primary purpose is to collect acid mist.

Unless there is some evidence to the contrary, fabric filters operating at air to cloth ratios of 2 to 3 can probably be assumed to comply with most existing air pollution regulations (based on weight only) provided bag integrity is maintained (this is not to imply that higher air to cloth ratios may not also be effective). Regulations aimed specifically at the submicron respirable particulate size range may require further investigation of filter performance, however.

Thermal and catalytic afterburners are the most effective control devices for organic emissions. Thermal afterburners can also be effective for combustible particulate, such as phthalic anhydride, though the proper operating conditions may be considerably different than those for vapors.

Where afterburners are used as emission control devices, it is often possible to determine compliance by inspecting the system. It must first be determined whether all possible sources of organic vapors are vented into the afterburner inlet. For thermal afterburners, a determination that both temperature and residence time are acceptable is sometimes sufficient to establish compliance. Temperatures of 1250 to 1450°F and residence times from 0.3 sec to 0.6 sec are commonly acceptable. For catalytic afterburners, compliance is somewhat more difficult to ascertain. Proof that a regular catalyst maintenance schedule has been adhered to as well as a measurement of operating temperature, or temperature rise across the catalyst bed, can suggest that a unit is in compliance, but only a measurement of discharge hydrocarbon concentration can confirm adequate performance.

C. Filling and Packaging

Some of the same comments apply to the filling and packaging areas as apply to the paint manufacturing area. Solvent vapors represent the principle emissions from this area. Any exposure of solvent-containing materials to air should be viewed as a potential source. Low reactivity, lack of odor nuisance potential or measurement of low emission rate are the grounds for demonstrating compliance.

A complete compliance survey should identify as potential sources all of those points at which process equipment is vented to the atmosphere, or at which the solid or liquid materials being processed are exposed to the air. These points are most conveniently noted on a flow diagram of the process in question. Each such point should be noted as:

1. Likely to be in compliance by virtue of the materials being handled having little tendency to become airborn, or
2. Being exempt from regulation as non-reactive, non-odor-causing vapors, or
3. Having measured emissions low enough to be in compliance or having adequate collection and/or disposal equipment for the particular materials involved.

Many potential sources may be found to be in compliance by virtue of face-value evidence of the types indicated. Other potential sources should be considered suspect and accepted source testing methods used to establish compliance.

CHAPTER 7

ECONOMICS OF EMISSION CONTROL

Specific among the goals of this study was the determination of financial impact of air pollution control on the paint industry. In order to accomplish this goal, the effort was subdivided into three parts as follows:

I. Cost of Best Control Equipment
II. Model Plant Study
III. Industry Wide Studies

These elements of the study are covered in the following pages.

I. COST OF BEST CONTROL EQUIPMENT

In order to develop current and accurate costs for best control as applied to the paint and varnish industry, a number of equipment manufacturers and the Industrial Gas Cleaning Institute were retained as subcontractors to furnish cost information.

The Industrial Gas Cleaning Institute (IGCI) is an association of air pollution equipment manufacturers and represents a majority of the larger suppliers to the marketplace. The IGCI has had considerable experience in supplying information of the type required in this study to the Federal Environmental Protection Agency in a number of "Air Pollution Control Technology and Costs" contracts. The IGCI was retained as a consultant in order to select the member companies most qualified to provide the required cost information. In addition to selecting companies, the Standards Committee of the IGCI was used to review and approve all technical information supplied in the study.

The IGCI member companies and equipment manufacturers selected were each supplied the following information:

1. Process narrative for the paint and varnish industry
2. Specifications for abatement equipment
3. Instructions for submitting cost data

4. Process descriptions for thermal and catalytic afterburners for a resin reactor and for an open kettle
5. Operating conditions for thermal or catalytic afterburners (with and without heat exchange) for large and small closed kettles; and (without heat exchange) for large and small open kettles
6. Data forms for estimated capital and annual operating cost

The process narrative and cost data forms (items 1 and 6 above) are included in this report as Appendix B and Appendix C, respectively. Other information supplied above (items 2 thru 5) follow as Tables 64 to 81 which can be found at the end of this chapter.

Based on information supplied, participating IGCI member companies furnished equipment bid information and estimates of erection or installation of the system required. According to instruction, the erection or installation estimates were based on a Milwaukee, Wisconsin location or an alternate city with a construction cost index near the national average. Therefore, the installation cost information presented was adjusted based on the cost indices presented in Table 82. This information was taken from *Building Construction Cost Data 1970** which presents a construction cost index for 90 cities using 100 to represent the national average. The indices presented are for the building trades only and are used as representative for general rates on field construction. Since the indices do not account for differences in labor productivity, the cost variations among cities may be understated.

Direct operating cost information was also provided for the best control equipment by the participating IGCI member companies. These costs were developed using estimated requirements and the following basis:

	Units	Unit Price	
Labor	Dollars/hour	$6.00	Operator
		$8.00	Supervisor
Maintenance materials	Dollars/year	Cost**	
Replacement parts	Dollars/year	Cost**	
Electric power	Dollars/kwh	$0.011	
Fuel	Dollars/MM Btu	$0.80	
Water (process)	Dollars/M gal	$0.25	
Water (cooling)	Dollars/M gal	$0.05	
Chemicals	Dollars/year		

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*Published by Robert Snow Means Company.

**See Appendix C.

With this information, annual operating costs were developed using direct costs estimated on the preceding plus an annual capital charge.

Cost information for fabric collectors was developed using equipment quotations and operating conditions obtained directly from equipment suppliers. In this manner, information was developed using a single air rate for the pulse test and shaker type fabric collectors. With this information, Air Resources, Inc., developed installation and operation cost estimates using the same bases as for the IGCI work. The estimate information is presented on the following page.

Capital and operating costs presented herein are based on 1972 dollar values. Caution should be exercised in using the cost information presented as a basis for preliminary estimates of air pollution control cost. Dollar values may require adjustment due to inflation and labor rates and productivity may require adjustment to prevailing conditions.

A. Thermal Afterburners

Process descriptions were developed as follows:

1. Thermal afterburner process description for resin reactor specification
2. Thermal afterburner process description for open kettle specification

Operating conditions were developed for the resin reactor case with and without the use of heat exchange. Operating conditions for the open kettle specification were developed without heat exchange.

The process description for Resin Reactor Specification is presented in Table 66. Related operating conditions of afterburners without heat exchange are presented in Tables 67 and 68. Similar conditions with heat exchange are presented in Tables 69 and 70.

The Process Description for Open Kettle Specification is presented in Table 71. Related operating conditions of thermal afterburners without heat exchange are presented in Tables 72 and 73.

Capital cost information shown in Figures at the end of this chapter was based upon the specification bid information as previously described. Capital cost information for thermal afterburners without heat exchange is presented in Figure 66. Similar cost information with heat exchange (42% efficient) is presented in Figure 67. Total installed costs for thermal afterburners are presented in Figure 68 and a comparison is presented with catalytic afterburners. This figure also compares systems with and without heat exchange.

Annual operating costs were developed using methods described previously. Figure 69 presents *direct* annual operating costs for thermal afterburners, without heat exchange, and also includes a comparison with catalytic afterburners. Similar information with heat exchange included is presented in Figure 71. Figure 70 presents *total* annual operating cost for thermal afterburners without heat exchangers and also includes a comparison with catalytic afterburners. Similar information with heat exchangers is presented in Figure 72.

B. Catalytic Afterburners

Process descriptions were developed for catalytic afterburners as shown:

1. Catalytic afterburner process description for resin reactor specification
2. Catalytic afterburner process description for open kettle specification

Operating conditions were developed for the resin reactor case with and without heat exchange. Operating conditions were developed for the open kettle without heat exchange.

The process description for resin reactor specification is presented in Table 74. Related operating conditions without heat exchange are presented in Tables 75 and 76. Similar conditions with heat exchange are presented in Tables 77 and 78.

The process description for open kettle specification is presented in Table 79. Related operating conditions without heat exchange are presented in Tables 80 and 81.

Capital cost information was developed based upon specification bid information as previously described. Capital cost information for catalytic afterburners without heat exchange are presented in Figure 64. Similar cost information with heat exchange (23% efficient) is presented in Figure 65. Total installed costs for catalytic afterburners are presented in Figure 68 and a comparison is presented with thermal afterburners. This figure also compares systems with and without heat exchange.

Annual operating costs were developed using methods described previously. Figure 69 presents *direct* annual operating costs for catalytic afterburners, without heat exchange, as well as comparative data for thermal afterburners. Similar information, with heat exchange, is presented in Figure 71.

C. Fabric Collectors

Cost of fabric collectors was estimated using a single case for pigment recovery. This was based on the following operation conditions:

Air handling rate, CFM	3,800
Pigment recovered, lb/yr	2,850

Using these conditions, air to cloth ratios were selected and cost information developed. This information is presented in Table 84.

II. MODEL PLANT STUDY

In order to develop current and accurate cost information for the paint and varnish industry, Air Resources, Inc. enlisted the assistance of the Sherwin-Williams Company as a subcontractor. The Sherwin-Williams Company is a large multiplant company in the paint and varnish industry and possesses a thorough knowledge of investment and operating costs for plants of the type considered herein.

As a basis for estimating costs for the Model Plant the following were established:

1. The plant site consists of a hillside location approximately 37 miles northwest of Chicago and in or around the city of Elgin, Illinois.
2. Land costs are not included in the estimate.
3. All required utilities are available at the property line.
4. Uniform Building Code, OSHA and National Fire Protection Association regulations are applied to the plant.
5. Construction costs are based on December, 1972 for the Chicago, Illinois, metropolitan area.

Using the above bases, capital costs were developed for the model plant along with balance sheets, operating statements and financial impact of control. These are discussed below.

A. Capital Cost of Plant

Using bases described previously, an estimate of capital investment was developed for the Model Plant. The estimate was based on an item-by-item cost breakdown which is presented in Appendix A of this report. The specific equipment selected for inclusion in the estimate is believed to be representative of that which might be installed in a plant of the model type. Certain of the equipment was selected based on accessability of information and does not necessarily represent the optimum or the lowest cost equipment that could be utilized. Inclusion of specific equipment items should not be considered to be an endorsement of any brand or model.

The total estimated cost for the Model Plant is $3,755,000. A summary of the cost items is presented in Table 95. In addition, Table 96 presents a summary of equipment and utility costs.

B. Balance Sheet and Operating Statement

In developing financial information for the uncontrolled plant, an attempt was made to utilize a realistic approach while at the same time trying to avoid unnecessarily complex handling and accounting situations. In order to simplify accounting, the model plant was assumed to be fully operational with start-up costs and investment credits having expired in a prior period. Labor availability, specific geographical raw material supply and geographical competitive market forces were not considered. All data is based upon the model with operations on a two-shift basis. With these bases, the following information was developed:

Table 85 — Annual Raw Material Requirements and Estimated Annual Costs
Table 86 — Annual Package and Package Material Requirements and Estimated Annual Costs
Table 87 — Annual Wage and Salary Estimated Costs
Table 88 — Annual Depreciation Costs
Table 89 — Income Statement Year Ending December 31, 19__2
Table 90 — Annual Production Schedule Detailed by Month Showing Sales and Inventory Levels
Table 91 — Balance Sheet at Year-end, December 31, 19__2
Table 92 — Cash Flow Statement for Year 19__2
Table 93 — Return on Investment Year 19__2
Table 94 — Annual Product Mix
Figure 73 — Factory Manning and Organization Chart

Discussion of the schedules are presented on the following pages.

Raw Materials (Table 85)

This schedule details the raw material requirements necessary to produce the product mix included in Table 94. The raw material prices used in this schedule are based upon vendor quotation and include delivery charges.

Packages and Associated Materials (Table 86)

Table 86 details the packages and associated materials to satisfy the product mix and the packaging schedule for the model plant.

Wages and Salaries (Table 87)

Table 87 establishes the wage and salaries estimates for the Model. These requirements were based upon the organization shown in Figure 72. While the salaries assumed may represent a very subjective viewpoint, these are thought to be representative. The hourly wage rate was calculated by using the average rate for SIC 2851 for 1971 from the *Statistical Abstract of the United States*, with a factor of 10 per cent added. For second shift requirements a shift differential of 10¢/hr was added. FICA taxes are calculated using current employer percentages. Fringes exclusive of FICA were estimated at 5 per cent of wage and salary cost.

Depreciation (Table 88)

Table 88 presents the depreciation costs associated with the model plant. The straight line method was used for calculating depreciation without deducting any salvage costs. The buildings were depreciated over an 80 year life and the equipment over a 10 year life.

Income Statement (Table 89)

This table was prepared based on several assumptions and estimates which include the following:

1. Selling price was developed using an average from the Current Industrial Reports M28F for 1971. The average from this report was increased 4 per cent for industrial shipments to adjust for growth rise.
2. Estimates were made for "other manufacturing costs" of 50¢/gal on trade shipments and 30¢/gal on industrial shipments. Industrial shipment costs are estimated lower since less operating cost is associated with the equipment and filling of large industrial packages.
3. The estimate used for selling, general and administrative expense are directed primarily at selling expense. For trade sales an estimate of 15 per cent of sales was used, and for the industrial products only 5%. The differences in these percentages reflect alternate levels of effort required by a small industrial manufacturer to service a specific industry (or at best several small manufacturers) compared to servicing a large number of retailers.

In addition, taxes, both federal and local, were estimated and these percentages are shown in the schedule.

Production Schedule (Table 90)

The table presents a detailed estimate breakdown by months of production, shipments and inventory. Also included is a safety reserve amounting to approximately 5 per cent of annual shipments.

Balance Sheet (Table 91)

In preparing the balance sheet, liabilities were recognized for taxes and accounts payable, but such items as prepaid expenses were specifically avoided.

Inventory accounts were developed using an average cost basis and the gallonage shown in ending inventory in Table 90 for December 31, 19__2.

Plant financing was assumed to consist of a capitalization of one million dollars and a bank loan of four million dollars over a ten-year term at 7 per cent interest.

The balance sheet shows negative cash which would indicate the need for at least seasonal borrowing currently. This solution would become less acute as interest expense decreases with long term debt.

Cash Flow Statement (Table 92)

A simplified cash flow statement is presented which assumes that no change occurs in accounts receivable, accounts payable and in inventory levels between years.

Return on Investment (Table 93)

Table 93 presents returns on investment calculations using four separate calculation techniques. These include the total gross assets available method, the total net assets available method, stockholders equity plus long term debt method and the stockholders equity method.

Product Mix (Table 94)

Table 94 shows the product mix assumed for model plant. Fifty per cent of the industrial output was selected by the subcontractors in preparing the table. Considering the size of the plant and the associated difficulties of manufacturing industrial finishes, the following mix was established:

	Gallons	Name
1.	95,000	Monomer modified alkyd for fast dry coatings
2.	95,000	Acrylic baking enamel
3.	190,000	Alkyd urea baking enamels
	380,000	50% of industrial output

C. Balance Sheet and Operating Statement for Controlled Plant

The balance sheet and operating statement for the controlled plant were prepared using the same assumptions and basis which were documented previously for the controlled plant. That financial information which is changed for the controlled plant solution is as follows:

Table 97 — Annual Depreciation Costs Including Air Emission Control Devices

Table 98 — Income Statement Year Ending December 31, 19__2 adjusted to show the effect of air emission control devices

Table 99 — Balance sheet at year-end, December 31, 19__2 adjusted to show the effect of air emission control devices

Table 100 — Cash flow statement year 19__2 adjusted to show the effect of air emission control devices

Table 101 — Return on investment year 19__2 adjusted to show the effect of air emission control devices

Table 102 — Financial information on recommended air emission control devices

Each table above is presented in respective order at the end of this chapter.

D. Cost of Control Other Than Add-on Equipment

The high costs associated with air pollution control in the paint industry invites consideration of alternative means for reduction of emission levels. Significant among these alternatives is the potential for raw material substitution and/or process modification.

1. Raw Material Substitution — Appreciable reduction in emissions of air pollutants can be achieved when it is possible to substitute raw materials with compounds which from an air pollution standpoint offer more desirable physical and chemical properties. The most beneficial choice for substitution is the solvent base of the paint since such materials represent the major source of emissions from paint plants. Paramount among the possibilities for solvent substitution is the use of water or the conversion to water base coatings. Where water based formulations can be developed to satisfy any of a variety of end uses, an order of magnitude of emission reduction is possible in the paint industry. This is not always easily accomplished since product quality must be maintained.

Significant progress has been made in the paint industry through the development of water emulsion trade sales paints. Many of these developments have been achieved without increase in cost or sacrifice in quality.

Current development work is underway on the use of dry powder paint formulations. Where such formulations will fulfill the end-use requirements, significant emission reduction is possible in not only production, but in paint application as well.

Another technology development which has great potential in reducing solvent emissions, particularly by the user, is the formulation of water reducible industrial coatings. Heretofore, the use of water based coatings has been restricted almost exclusively to trade sales products. In the opinion of some experts, use of such industrial coating systems will come to fruition before powder coatings.

Use of high solids systems is a further area for potential improvement. The net result of this approach is to reduce the amount of solvent present per unit coverage of the applied coating. Consequently, solvent emissions by the user will be reduced.

Good potential exists for reduction in the quantity of undesirable emissions using either alternative solvents or preparations which entirely eliminate the use of solvents. While considerable development work remains to be accomplished in the *"no-solvent"* area, a significant effort has been expended toward the substitution of alternative solvent materials. Much of this effort has been devoted to substitution with *"non-photochemically"* reactive solvents. This latter work has been very successful and a significant switch is now underway or being contemplated by the industry. Such conversions are resulting in sizeable reductions in photochemically reactive emissions by both the manufacturer and the user.

Aside from consideration of solvents, potential exists for emission level reduction through substitution of other constituents in the paint formulation. Use of the liquid instead of the solid form of certain raw materials, e.g., phthalic anhydride (PA) in resin manufacture, can result in reduced emissions. This is economically feasible when large quantities are being used. Introduction of liquid materials eliminates the necessity for evacuation of the equipment during loading operations. In the case of phthalic anhydride the potential for emission is transferred to another point in the process when the liquid form is used. Emission potential exists at the heated PA storage tank vent. Such emission can be easily controlled, however, by venting the storage tank through a water jacketed vertical condenser with provisions for admitting steam to the jacket. The tank is blanketed with inert gas and appropriate pressure relief control provided. During loading the water cooled condenser collects PA vapors as a solid which is later melted and returned to the storage tank.

Raw material substitution as outlined above can provide an excellent and sometimes inexpensive method for emission reduction by the manufacturer. Unfortunately, these benefits may not necessarily accrue to the users since raw material substitution can lead to both higher costs and lower quality. An example of this which is unrelated to air pollution is the product deterioration which has occurred as the result of the elimination of mercury fungicides and lead drying agents. Industry spokesmen point out in this latter case that a period as long as several years may be required to develop substitute raw materials which will restore paint to its former quality.

In many cases to date where raw material substitution has been made, the net result has been either a higher product cost and/or a lower quality product. It is the conclusion of some paint manufacturers that it would be less expensive overall for their customers to add control equipment for existing solvent emissions than to absorb the cost for special solvent systems. This factor coupled with the potential for degradation in product quality as well as the possibility for future regulatory changes, e.g., the exempt solvent definition, suggest that raw material substitution should be carefully evaluated as an alternative means for control.

2. Process Modification — Some potential exists for reduction in emission through process modification. Possible modification includes:

a. Reduction in use of sparge gases
b. Use of adequate or refrigerated condensers
c. Use of proper unloading and transfer methods
d. Use of liquid slurries in pigment handling

Taking maximum advantage of these modifications can substantially reduce emissions in some operations such as resin cooking by the solvent method. The actual benefits to be derived depend on the specific operation involved and should be subjected to a cost/benefit analysis in relation to corresponding requirements and costs for air pollution control.

E. Varying Types and Levels of Control

Varying types and levels of control can be achieved with the thermal or catalytic afterburner segments of the air pollution control system for the paint plant. However, significant cost variations will be encountered which are dependent on the variation in control desired.

For example, suppose a hypothetical thermal afterburner is operating at an outlet temperature of 1370°F obtained from a burner ΔT from fuel gas of 550°F and a fume combustion efficiency of 90%. If the burner ΔT is increased by 50°F, the efficiency might, for some fumes, increase to 95% and give an outlet temperature of 1450°F. For a situation with these parameters, this variation in control level would result in an increase in fuel costs of around 9% without heat exchange. For the same afterburner to which 42% heat exchange has been added, the same increase in control level would result in an increase in fuel cost that would be less in actual dollars than the increase for the first case but could amount to about 30% of the fuel cost of the heat exchanged afterburner before increasing the temperature.

In the increased efficiency case above, additional maintenance costs would be encountered. This arises from increased maintenance resulting from higher temperature. This maintenance increase is not an easily assignable cost on afterburners since the number of start-ups and shutdowns influence this cost markedly. For the same operation cycle, however, maintenance cost will be significantly higher for the heat exchanger case and will partially offset the lower fuel cost indicated above.

Other operating costs for higher efficiency operation in the thermal afterburner will not be significant. Slight increase in fan horsepower requirements, however, might be involved. Operating labor requirements should be identical for either the high or low efficiency case.

Higher efficiency levels in baghouse operations are not readily obtainable since these systems already operate at 99+ per cent efficiency (weight basis) when the system is in good working order. Regular maintenance and observation will maintain these systems at very high levels of efficiency.

F. Impact on Income, Cash Flow and Investment

The impact of air pollution control costs for the paint industry will be significant. Basing an assessment of this impact on the model plant described previously, the following comparison may be made between the controlled and uncontrolled plants:

ANNUAL INCOME STATEMENT

	Uncontrolled plant	Controlled plant	Change for controlled plant
Revenue (net)	$6,604,400	$6,604,400	—
Cost of goods sold	5,020,374	5,029,602	+ 9,228
Gross profit	$1,584,026	$1,574,798	$ − 9,228
Selling, general and admin. expense	761,141	761,141	—
Operating income	$ 822,885	$ 813,657	$ − 9,228
Interest expense	252,000	254,101	+ 2,101
Income before taxes*	$ 570,885	$ 559,556	$ − 11,329
Income taxes	342,531	335,733	− 6,798
Net income	$ 228,354	$ 223,823	$ − 4,531

*Includes local, state and federal taxes.

This information indicates a reduction in annual income after tax of $4,531 for the addition of air pollution control equipment to the model plant. This loss in income amounts to 1.98 per cent of the total net income of the model plant or an average of $0.006 per gallon of paint produced.

The information above regarding loss of income is based on the assumption that the model plant would not encounter a price increase as a result of the effect of control on its supplier of purchased resins. Of the 8,115,300 pounds of resin used by the model plant, 1,992,600 pounds of solvent based resins are purchased from outside suppliers. A significant portion of the control cost is directly attributable to resin manufacture. The design basis for manufactured resin incorporates a production capacity of 2,166,000 pounds annually. The average capital cost of control for the resin plant has been shown previously as $26,000. The operating cost attributable to control on the model resin plant at design capacity is as follows:

INCREASED ANNUAL MANUFACTURING COST OF RESIN RESULTING FROM CONTROL

Depreciation (installed cost)	$2,600
Annual operating cost	5,595
Decrease in operating income	$8,195
Interest expense (assumed 7%)	1,638
Decrease in pretax income	$9,833
Tax reductions (Federal & Local)	5,900
Decrease in net income	$3,933

Applying this reduction in net income to the 2,166,000 pounds of resin used as the design basis, the model plant will show increased production and interest costs of $0.00182 per pound of resin. With the assumption that the outside resin supplier would incur the same increase in per pound cost and pass this along as a cost increase, the loss in income to the model plant would be increased significantly. Applying the $0.00182 per pound cost increase to 1,992,600 pounds of resin purchased would increase income loss by $3,626.53 annually or to $0.00191 per gallon of paint produced. This assumes that production of water based latex resins do not require equivalent control devices.

While the assumption made above for *purchased resin cost increase* is rather general, the order of magnitude of increase deserves consideration in all of the financial calculations relating to best control. Therefore, in the following financial data the influence of this factor will be pointed as an effect of *purchased resin cost increase*.

Effect of control on cash flow also is significant. Based on information previously presented for the model plant, the following comparison can be made:

NET CASH FLOW (ANNUALLY)

	Net cash flow
Uncontrolled plant	($ 14,512)
Controlled plant	(19,043)
Change in cash flow	($ 4,531)

While a cash out flow is indicated for each case, the cash out flow will be increased by $4,531 for the addition of control equipment. The negative cash flow calculated suggests that some seasonal short-term financing would be necessary to furnish cash requirements and that such debt would be increased for the controlled plant case.

Each of several methods for assessment of return on investment illustrates the impact of addition of air pollution control. These methods of calculation and the resultant conclusions have been shown previously for the model plant. A summary of the calculations is as follows:

RETURN ON INVESTMENT (PER CENT)

	Uncontrolled plant	Controlled plant	Change for controlled plant
Total gross assets	6.53%	6.42%	−1.68%
Total net assets	6.96%	6.85%	−1.58%
Stockholders' equity plus long-term debt	7.55%	7.43%	−1.59%
Stockholders' equity	19.70%	19.36%	−1.73%

The largest impact indicated from this summary is on the owners of the business or the stockholders. Based on stockholders' equity, approximately a 1.73% reduction in annual return results from the control additions.

Assuming a *purchased resin cost increase* as outlined previously, a reduction in income of $3,627 would be encountered with a resultant $220,196 annual income. With this reduced income, the loss of return on stockholders' equity for the controlled situation would be 19.04%. On this basis, the net reduction in return based on stockholders' equity would be 3.25%.

III. INDUSTRY WIDE STUDIES

An assessement of the impact of best control on an industry wide basis can be made using the following assumptions:

1. "Best Control" will be a requirement for all plants.
2. Cost of control is directly proportioned to overall production rates, i.e., the model plant represents the average plant.

While these assumptions present certain inaccuracies, they should permit a reasonable estimate of the order of magnitude of control cost. With these above assumptions, the industry wide influences are reviewed below:

A. Present Total Cost to Industry to Meet Best Control Requirements

Paint production during 1972 was at a level of 930 million gallons per year. A reasonable basis for estimating the order of magnitude of total cost to industry to meet best control might use the capital and operating costs developed for the model plant above on the basis of cost per gallon. With this basis, the approximate costs can be calculated as shown on the following page.

TOTAL COST TO INDUSTRY FOR BEST CONTROL

	Total Cost
Capital Investment Cost	$16,200,000
Annual Operating Cost*	$ 4,500,000

*OPERATING COSTS PLUS DEPRECIATION
In the case of capital investment cost, the above does not reflect a credit for any existing air pollution control equipment. The cost information presented is based on 1972 monetary values, costs and productivity and does not provide escalation factors.

B. Fifteen Year Projection of the Cost of Control

Indicated above was a 1972 paint production rate of 930 million gallons per year. Most of this production was accounted for by a relatively small number of plants. Paint production is projected to increase to 1,320 million gallons per year in 1985. Extrapolating beyond 1985, total annual paint production could exceed 1,700 million gallons per year.

Approximately 20% of the total operating plants produce about 85% of all coatings. The industry trend is toward larger plants combined with a tendency to operate these plants on a three-shift or 24-hour basis. This trend is expected to continue with the result that most increases in production will be due to the installation of new plants of large capacity or by full utilization of presently idle capacity rather than by increasing the operating hours.

Whether new plants or idle capacity are utilized, air pollution control requirements would need to increase beyond the minimum necessary for today's production. A reasonable basis for estimating the order of magnitude of future control costs might include an extrapolation of cumulative capital cost and annual operating cost as a function of the projected industry shipment. This extrapolation could be based on a proportionate cost per gallon of paint equal to that for the model plant based on 1972 cost factors. This extrapolation provided the following estimate of projected costs:

PROJECTED COST OF CONTROL (15 YEAR PERIOD)

	Total Cost
Capital Investment Cost	$30,600,000
Annual Operating Cost*	$ 8,500,000

*BASED ON 1,700 MILLION GALLONS PAINT PRODUCTION EACH YEAR
These estimates are based upon 1972 dollars. Changes in cost due to inflation, labor productivity, increased taxes, and other factors could easily swell the above total by a factor of two or more.

C. Sources of Capital For Pollution Control

Projections of capital investment based on the model plant suggest that, at present, on the order of 16 million dollars in expenditures is required to provide best air pollution control. Further projections suggest that at least 30.6 million will need to be expended in the 15 year period after 1972. This represents a substantial capital requirement on the particular industry and the optimum method of financing will be dependent on some of the following variables:

1. Business condition of the specific paint manufacturer
2. Money market or interest rates
3. Strength of the equity market
4. National monetary valuation and controls

In the reasonable future, those manufacturers representing the majority of production will all probably utilize the following sources of capital:

1. Retained earnings
2. Long-term borrowing or bonds
3. Portions of new equity capital

The financing technique used will in all likelihood result in an increase in the debt/equity ratios for the industry.

Accelerated tax credits and accelerated depreciation allowances are expected to be important factors in offsetting a portion of the capital requirements. It is anticipated, however, that eventually the cost of control will be absorbed in price increases to the extent that competition from other coatings or construction materials will allow.

D. Industry Structure

The paint industry has an oligopolistic structure. That is to say, the majority of production is controlled by relatively few companies. Approximately 1,727 paint plants were being operated in the United States during 1972. These plants were either directly owned or controlled by 1,365 U.S. companies. This does not include those plants which make paint components only, such as resins, but not finished coatings.

As indicated previously, about 20% of the total number of plants, or 345, produce about 75% of the total paint production. This 75% of total production is controlled by fewer than 200 companies which, in turn, control some of the smaller plants. The distribution of paint production among controlling companies is approximately as follows:

DISTRIBUTION OF PAINT PRODUCTION[1,7]

	Number of Companies	Approximate Percentage of Total Production
Major Companies	36	64
Intermediate Companies	164	24
Small Companies	1,165	12
	1,365	100.0

The above confirms that the paint industry has an oligopolistic structure.

In spite of this structure, the coatings business is probably unique among major manufacturing industries in that the very small producer is able to survive in the face of competition from some of the largest corporations in the world. While the trend is towards larger plants, it is a slow process and the continued existence of the small producer is assured for the foreseeable future. There are several reasons for this:

1. The diversity of products is so large that there will always be a place for the producer of low volume specialty items.
2. Finished coatings are expensive to ship due to their weight and volume. Consequently, the economy benefits of large operations are diminished as the shipping distance is increased.
3. A large amount of technical assistance is available from raw material suppliers which enables the small company to remain technologically up-to-date.
4. The nature of the manufacturing operations (batch processing of relatively small quantities) limits the economy that can be attained in large scale operations. Indeed, with the possible exception of filling and warehousing operations, there is little difference in the manner in which the small plant does things as opposed to the way large plants operate.

E. Product Elasticity — Production Substitution

The paint industry continues to demonstrate an upward growth pattern. This growth continues even during periods of rapidly increasing prices. The industry exhibits a strong indication of price inelasticity, i.e., demand and total receipts do not significantly change with rising prices. In the case of increasing prices, the separation of "real" and inflationary related contributions is difficult. In the case of price increases associated with air emission control devices, little if any effect on demand inelasticity can be projected.

Future increases in price will be influenced by a number of cost factors only one of which is projected air pollution control costs. Perhaps more significant to the paint industry will be cost increases from the following areas:

1. Inflation
2. Labor productivity reduction and cost increase
3. Energy cost increases
4. Water treatment and solid waste disposal costs
5. OSHA regulations

Also to be considered in price increase is product reformulation in terms of quality or of pollution control requirements of the user.

Product substitution is also a significant factor in the present era of rapid technological growth. Product substitution has been significant in recent years in the following areas:

1. Wall coverings
2. Paneling
3. Plastics

It is anticipated that a high level of product substitution will continue in the above areas and extend into other areas. However, for the foreseeable future, it is not anticipated that air pollution control costs alone will cause a substantial increase in product substitution.

TABLE 64

SPECIFICATIONS FOR ABATEMENT EQUIPMENT

1. SCOPE

A. This specification covers vendor requirements for air pollution control equipment for the subject process. The intent of the specification is to describe the service as thoroughly as possible so as to secure vendor's proposal for equipment which is suitable in every respect for the service intended. Basic information is tabulated in sections 2 and 3. The vendor should specify any of the performance characteristics which cannot be guaranteed without samples of process effluent.

B. The vendor shall submit a bid showing three separate prices as described below.

1. All labor, materials, equipment and services to furnish one pollution abatement device together with the following:
    - a. All ladders, platforms and other accessways to provide convenient access to all points requiring observation or maintenance
    - b. Foundation bolts as required
    - c. Six (6) sets of drawings, instructions, spare parts list, etc., pertinent to the above
2. Auxiliaries including:
    - a. Fan(s)
    - b. Pump(s)
    - c. Damper(s)
    - d. Conditioning Equipment
    - e. Dust Disposal Equipment
3. A turnkey installation of the entire system including the following installation costs:
    - a. Engineering
    - b. Foundations & Support
    - c. Ductwork
    - d. Stack
    - e. Electrical
    - f. Piping
    - g. Insulation
    - h. Painting
    - i. Startup

TABLE 64 (continued)

- k. Performance Test
- l. Other (including general tradework such as erection, rigging, etc.)

C. For the "pollution abatement device only" quotation, the vendor shall furnish the equipment FOB point of manufacture, and shall furnish as a part of this project competent supervision of the erection, which shall be by others.

D. Vendor shall furnish* the following drawings, etc., as a minimum:

1. With his proposal:
    - a. Plan and elevation showing general arrangement
    - b. Typical details of collector internals proposed
    - c. Data relating projected performance with respect to pressure drop, gas absorption efficiency and particulate removal efficiency to operating parameters such as gas flow
2. Upon receipt of order:
    - a. Proposed schedule of design and delivery
3. Within 60 days of order:
    - a. Complete drawings of equipment for approval by customer
4. 30 days prior to shipment:
    - a. Certified drawings of equipment, six sets
    - b. Installation instructions, six sets
    - c. Starting and operating instructions, six sets
    - d. Maintenance instructions and recommended spare parts lists, six sets

E. The design and construction of the collector and auxiliaries shall conform to the general conditions given in Section 5, and to good engineering practice.

2. PROCESS PERFORMANCE GUARANTEE

A. The equipment will be guaranteed to reduce the particulate and/or gas contaminant loadings as indicated in the service description.

B. Performance test will be conducted in accordance with IGCI test methods where applicable.

C. Testing shall be conducted at a time mutually agreeable to the customer and the vendor.

D. The cost of the performance test is to be included in vendor's turnkey proposal.

*This is a typical request. The member companies are NOT to furnish this material under the present project.

TABLE 64 (continued)

E. In the event the equipment fails to comply with the guarantee at the specified design conditions, the vendor shall make every effort to correct any defect expeditiously at his own expense. Subsequent retesting to obtain a satisfactory result shall be at the vendor's expense.

3. GENERAL CONDITIONS

A. Materials and Workmanship

Only new materials of the best quality shall be used in the manufacture of items covered by this specification. Workmanship shall be of high quality and performed by competent workmen.

B. Equipment

Equipment not of vendor's manufacture furnished as a part of this collector shall be regarded in every respect as though it were of vendor's original manufacture.

C. Compliance with Applicable Work Standards and Codes

It shall be the responsibility of the vendor to design and manufacture the equipment specified in compliance with the practice specified by applicable codes.

D. Delivery Schedules

The vendor shall arrange delivery of equipment under this contract so as to provide for unloading at the job site within a time period specified by the customer. Vendor shall provide for expediting and following shipment of materials to the extent required to comply with delivery specified.

TABLE 65

INSTRUCTIONS FOR SUBMITTING COST DATA

Two forms (two copies each) are enclosed with each specification. These are for submitting:

(A) Estimated Capital Cost Data

(B) Annual Operating Cost Data

These forms will also be used to exhibit averages of the three cost estimates for each process and equipment type. Because your costs will be averaged with those of other IGCI members, it is necessary to prepare them in accordance with instructions given in the following paragraphs.

(A) Estimated Capital Cost Data

The upper part of this form should already be filled out for the particular application when you receive it. This information on operating conditions should be identical to that in the specification and is repeated here only for the convenience of those reading the form.

You should fill in the dollar amounts estimated in the appropriate spaces on the bottom half of the form. It should not be necessary to add any information other than the dollar amounts. If you wish to provide a description of the equipment proposed, please do so on one or more separate sheets of paper, and attach it to the form. If any item is not involved in the equipment you are proposing, please indicate this by writing "none" in the space rather than leaving it blank or using a zero.

(1) The "gas cleaning device" cost should be reported just as you would report a flange-to-flange equipment sale to the IGCI. That is, a complete device including necessary auxiliaries such as power supplies, mist eliminators, etc. Do NOT include such items as fans, solids handling equipment, etc., unless these are an *integral part of your gas cleaning device*.

(2) "Auxiliaries" are those items of equipment which are frequently supplied with the gas cleaning device. There is a purely arbitrary definition of those items included here and those included in the "Installation" Costs. Do NOT include any of the cost of erecting or installing auxiliaries in this category.

(3) "Installation Cost" should include all of the material not in (1) or (2) and the field labor required to complete a turnkey installation. In cases where the equipment supplier ordinarily erects the equipment but does not supply labor for foundations, etc., it is necessary to include an estimated cost for these items. General tradework, including rigging, erection, etc. should be included in the "Other" category.

TABLE 65 (continued)

The installation should be estimated for a new plant, or one in which there are no limitations imposed by the arrangement of existing equipment. Installation labor should be estimated on the basis that the erection will take place in an area where labor rates are near the U.S. average, and the distance from your plant is no more than 500 miles. Milwaukee, Wisconsin is an example of a city with near-average labor rates.

(B) Annual Operating Cost Data

Some of the information will be supplied by Air Resources, such as unit costs for labor and utilities, and annualized capital charges. You should fill in the usage figures for the complete abatement system in the units indicated below. Please include the unit price.

Labor	hr/year
Maintenance Materials	\$/year
Replacement Parts	\$/year
Electric Power	kw-hr/year
Fuel	MMBtu/year
Water (Process)	MM gal/year
Water (Cooling)	MM gal/year
Chemicals	\$/year

Air Resources will average the consumption figures reported, and convert them to dollar values for inclusion in the final report.

Be sure that the operating factor, in hours per year, supplied by ARI, is used for estimating the utility and labor requirements.

TABLE 66

THERMAL AFTERBURNER PROCESS DESCRIPTION

FOR RESIN REACTOR SPECIFICATION

This specification describes the requirements for a thermal combustion system for abatement of the hydrocarbon emissions from the resin production facility of a paint and varnish plant. The system will be similar to that shown in Figure 9. All reactor thinning tanks and product rundown tanks will be vented to the collection system. Dilution air will be supplied through a hood over the resin filter press(es). A minimum flow damper is to be supplied in this part of the ventilation system. It is to be sized to allow for a maximum fume concentration of 40% LEL in the fully closed position. A high velocity Venturi section is to be located at the afterburner inlet to assure gas flow is in excess of flame propagation velocity at 1/2 design flow rate.

The afterburner is to be natural gas fired. Sufficient gas, having a specific gravity of 0.60 and an upper heating value of 1040 Btu/SCF, is available at a pressure of 1.0 psig.

The exhaust gas contains sufficient oxygen, greater than 16% O_2, to allow firing of the afterburner with a raw gas or process air burner. A combustion air system is not required. Fume load to the incinerator is composed of 75% kettle emission and 25% from other sources. Average emissions are 60% of peak. The system is to be designed on peak emission but operating costs are to be based on average emissions. Operating conditions listed are based on peak emissions. Fume destruction in burner is to be calculated as follows:

10% for catalytic units with or without heat exchange

10% for thermal units with heat exchange

20% for thermal units without heat exchange

Please fill in estimated efficiency of afterburner and burner duty.

The afterburner is to be supplied with a suitable control panel and all equipment is to be designed for outdoor operation. Incinerator operating and safety controls are to be designed to meet F.I.A. (Factory Insurance Association) requirement. All dampers are to be pneumatically operated and contain an integral fail safe air reservoir. The system is to automatically divert in the event of low flow, high afterburner temperature, high reactor pressure, and afterburner preheat burner failure. The exhaust system should also be purged with inert gas on fan failure or loss of flow. Damper operating is to be sequential with the position switches mounted on the damper arm and not the operator. The system fan shall be located after the preheat burner or the incinerator outlet and shall be constructed to withstand 200°F higher than design operating temperature. The fan shall have a vee belt drive and fan and motor shall have the capacity to overcome the pressure drop of the ductwork, afterburner and any heat exchanger that may be used. System ductwork should be sized for a maximum ΔP of 2 in. w.c. hot. The fan motor may be sized for restricted flow cold start. The ductwork to the incinerator should be heated either by the use of a double manifold or hot gas recycle or a combination of both.

The heat exchanger when included is to be the parallel flow shell and tube type and designed to operate at an afterburner outlet temperature of 1500°F. Maximum exchanger pressure drop, both sides, should not exceed a total of 6 in. w.c. hot. Dirty gas is to flow through the tube side.

TABLE 66 (Continued)

INSTALLATION

A complete turnkey proposal including ductwork, structural steel, fuel and inert gas piping, etc., is requested. For the purpose of this proposal fan and damper including operators are to be considered as auxiliary. The controls and control cabinet are to be included with the afterburner price. The afterburner will be assumed to be located on a structural steel base on the resin plant roof. No modification to the building structural steel is required. A tie through the roof from the base to the building steel is required. The base and tie in are part of the installed structural cost. All utilities are available within 30 ft of the control cabinet, motor, and burner. Plant air is available at 100 psig and located within 30 ft. Inert gas is available and will require 30 ft of piping from supply to ductwork. The existing stack can be used for the diversion stack. A 10 ft exhaust stack will be mounted on the afterburner, double manifold or exhaust fan. A total of thirty-five (35) feet of new exhaust ductwork and twenty-five (25) feet of double manifold will be required.

TABLE 67

THERMAL AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION
(Without Heat Exchange)

	Small	Large
Process Conditions		
Reactors, Number	1	2
Size each, gal	1,700	5,000
Hcbn Emission Max, lb/hr	42.4	254
Hcbn Emission Ave, lb/hr	24.7	148
Total Exhaust Rate, SCFM	1,000	6,000
Exhaust Temperature, °F	110	110
Heat of Combustion of Reactor Fume, Btu/lb	17,000	17,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Unit Residence Time, sec @ 1500°F	0.6	0.6
Afterburner Without Heat Exchange		
Unit Inlet, °F	325	325
Burner ΔT from Fuel Gas, °F	550	550
* Burner ΔT from Flame Combustion, °F	125	125
Burner Outlet Temperature, °F	1,000	1,000
** Unit ΔT from Thermal Combustion, °F	435	435
Unit Outlet Temperature, °F	1,435	1,435
Burner Duty, MM Btu/hr	——	——
Estimated Unit Removal Efficiency	——	——

* Assumes 20% fume combustion in burner flame
** Assumes 95% overall fume combustion

TABLE 68

THERMAL AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION

(Without Heat Exchange)

	Small	Large
Process Conditions		
Reactors, Number	1	3
Size each, gal	5,000	5,000
Hcbn Emission Max, lb/hr	125	423
Hcbn Emission Ave, lb/hr	74	246
Total Exhaust Rate, SCFM	3,000	10,000
Exhaust Temperature, °F	110	110
Heat of Combustion of Reactor Fume, Btu/lb	17,000	17,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Unit Residence Time, sec @ 1500°F	0.6	0.6
Afterburner Without Heat Exchange		
Unit Inlet, °F	325	325
Burner ΔT from Fuel Gas, °F	550	550
*Burner ΔT from Flame Combustion, °F	125	125
Burner Outlet Temperature, °F	1,000	1,000
**Unit ΔT from Thermal Combustion, °F	435	435
Unit Outlet Temperature, °F	1,435	1,435
Burner Duty, MM Btu/hr	——	——
Estimated Unit Removal Efficiency	——	——

* Assumes 20% fume combustion in burner flame

** Assumes 95% overall fume combustion

TABLE 69

THERMAL AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION
(With Heat Exchange)

	Small	Large
Process Conditions		
Reactors, Number		*2*
Size each, gal		*5,000*
Hcbn Emission Max, lb/hr		*254*
Hcbn Emission Ave, lb/hr		*148*
Total Exhaust Rate, SCFM		*6,000*
Exhaust Temperature, °F		*110*
Heat of Combustion of Reactor Fume, Btu/lb		*17,000*
Hydrocarbon Concentration Maximum, Btu/SCF		*12*
Average, Btu/SCF		*7*
Unit Residence Time, sec @ 1500°F		*0.6*
Afterburner with Heat Exchange		
Inlet Tube Side, °F		*325*
Unit Inlet, °F		*825*
Burner ΔT from Fuel Gas, °F		*115*
* *Burner ΔT from Flame Combustion, °F*		*60*
Burner Outlet Temperature, °F		*1,000*
** *Unit ΔT from Thermal Combustion, °F*		*500*
Unit Outlet Temperature, °F		*1,500*
Outlet Shell Side, °F		*1,030*
Burner Duty, MM Btu/hr		——
Exchanger Duty, MM Btu/hr		——
Thermal Efficiency		*~42%*
Overall Heat Trans. Coef., U		——
Tube Surface Area, ft²		——
Estimated Afterburner Removal Efficiency		——

* *Assumes 10% fume combustion in burner flame*
** *Assumes 95% overall fume combustion*

TABLE 70

THERMAL AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION
(With Heat Exchange)

	Small	*Large*
Process Conditions		
Reactors, Number	1	3
Size each, gal	5,000	5,000
Hcbn Emission Max, lb/hr	127	423
Hcbn Emission Ave, lb/hr	74	246
Total Exhaust Rate, SCFM	3,000	10,000
Exhaust Temperature, °F	110	110
Heat of Combustion of Reactor Fume, Btu/lb	17,000	17,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Unit Residence Time, sec @ 1500°F	0.6	0.6
Afterburner with Heat Exchange		
Inlet Tube Side, °F	325	325
Unit Inlet, °F	825	825
Burner ΔT from Fuel Gas, °F	115	115
* *Burner ΔT from Flame Combustion, °F*	60	60
Burner Outlet Temperature, °F	1,000	1,000
** *Unit ΔT from Thermal Combustion, °F*	500	500
Unit Outlet Temperature, °F	1,500	1,500
Outlet Shell Side, °F	1,030	1,030
Burner Duty, MM Btu/hr	——	——
Exchanger Duty, MM Btu/hr	——	——
Thermal Efficiency	~42%	~42%
Overall Heat Trans. Coef., U	——	——
Tube Surface Area, ft²	——	——
Estimated Afterburner Removal Efficiency		

* *Assumes 10% fume combustion in burner flame*

***Assumes 95% overall fume combustion*

TABLE 71

THERMAL AFTERBURNER PROCESS DESCRIPTION

FOR OPEN KETTLE SPECIFICATION

This specification describes the requirements for a thermal combustion system for abatement of the hydrocarbon emissions from the resin production facility of a paint and varnish plant. The system will be similar to that shown in Figure 9. All reactor thinning tanks and product rundown tanks will be vented to the collection system. Dilution air will be supplied through a hood over the resin filter press(es). A minimum flow damper is to be supplied in this part of the ventilation system. It is to be sized to allow for a maximum fume concentration of 40% LEL in the fully closed position. A high velocity Venturi section is to be located at the afterburner inlet to assure gas flow is in excess of flame propagation velocity at 1/2 design flow rate.

The afterburner is to be natural gas fired. Sufficient gas, having a specific gravity of 0.60 and an upper heating value of 1040 Btu/SCF, is available at a pressure of 1.0 psig.

The exhaust gas contains sufficient oxygen, greater than 16% O_2 to allow firing of the afterburner with a raw gas or process air burner. A combustion air system is not required. Fume load to the afterburner is composed of 75% kettle emission and 25% from other sources. Average emissions are 60% of peak. The system is to be designed on peak emission but operating costs are to be based on average emissions. Operating conditions listed are based on peak emissions. Fume destruction in burner is to be calculated as follows:

10% for catalytic units with or without heat exchange

10% for thermal units with heat exchange

20% for thermal units without heat exchange

Please fill in estimated efficiency of afterburner and burner duty.

The afterburner is to be supplied with a suitable control panel and all equipment is to be designed for outdoor operation. Afterburner operating and safety controls are to be designed to meet F.I.A. (Factory Insurance Association) requirement. All dampers are to be pneumatically operated and contain an integral fail safe air reservoir. The system is to automatically divert in the event of low flow, high afterburner temperature, high reactor pressure, and afterburner preheat burner failure. The exhaust system should also be purged with inert gas on fan failure or loss of flow. Damper operating is to be sequential with the position switches mounted on the damper arm and not the operator. The system fan shall be located after the preheat burner or the afterburner outlet and shall be constructed to withstand 200°F higher than design operating temperature. The fan shall have a vee belt drive and fan and motor shall have the capacity to overcome the pressure drop of the ductwork, afterburner and any heat exchanger that may be used. System ductwork should be sized for a maximum ΔP of 2 in. w.c. hot. The fan motor may be sized for restricted flow cold start. The ductwork to the afterburner should be heated either by the use of a double manifold or hot gas recycle or a combination of both.

The heat exchanger when included is to be the parallel flow shell and tube type and designed to operate at an afterburner outlet temperature of 1500°F. Maximum exchanger pressure drop, both sides, should not exceed a total of 6 in. w.c. hot. Dirty gas is to flow through the tube side.

TABLE 71 (Continued)

INSTALLATION

A complete turnkey proposal including ductwork, structural steel, fuel and inert gas piping, etc., is requested. For the purpose of this proposal fan and damper including operators are to be considered as auxiliary. The controls and control cabinet are to be included with the afterburner price. The afterburner will be assumed to be located on a structural steel base on the resin plant roof. No modification to the building structural steel is required. A tie through the roof from the base to the building steel is required. The base and tie in are part of the installed structural cost. All utilities are available within 30 ft of the control cabinet, motor, and burner. Plant air is available at 100 psig and located within 30 ft. Inert gas is available and will require 30 ft of piping from supply to ductwork. The existing stack can be used for the diversion stack. A 10 ft exhaust stack will be mounted on the afterburner, double manifold or exhaust fan. A total of thirty-five (35) feet of new exhaust ductwork and twenty-five (25) feet of double manifold will be required.

TABLE 72

THERMAL AFTERBURNER OPERATING CONDITIONS

FOR OPEN KETTLE SPECIFICATION
(Without Heat Exchange)

	Small	Large
Process Conditions		
Kettles, Number	2	4
Size each, gal	300	300
Hcbn Emission Max, lb/hr	45	90
Hcbn Emission Ave, lb/hr	26.2	52
Total Exhaust Rate, SCFM	1,000	2,000
Exhaust Temperature, °F	80	80
Heat of Combustion of Kettle Fume, Btu/lb	16,000	16,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Unit Residence Time, sec @ 1500°F	0.6	0.6
Afterburner Without Heat Exchange		
Unit Inlet, °F	300	300
Burner ΔT from Fuel Gas, °F	575	575
* Burner ΔT from Flame Combustion, °F	125	125
Burner Outlet Temperature, °F	1,000	1,000
** Unit ΔT from Thermal Combustion, °F	435	435
Unit Outlet Temperature, °F	1,435	1,435
Burner Duty, MM Btu/hr	——	——
Estimated Unit Removal Efficiency	——	——

* Assumes 20% fume combustion in burner flame

** Assumes 95% overall fume combustion

TABLE 73

THERMAL AFTERBURNER OPERATING CONDITIONS

FOR OPEN KETTLE SPECIFICATION

(Without Heat Exchange)

	Small	*Large*
Process Conditions		
Kettles, Number	1	6
Size each, gal	300	300
Hcbn Emission Max, lb/hr	22.5	135
Hcbn Emission Ave, lb/hr	13.1	78.8
Total Exhaust Rate, SCFM	500	3,000
Exhaust Temperature, °F	80	80
Heat of Combustion of Kettle Fume, Btu/lb	16,000	16,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Unit Residence Time, sec @ 1500°F	0.6	0.6
Afterburner Without Heat Exchange		
Unit Inlet, °F	300	300
Burner ΔT from Fuel Gas, °F	575	575
* *Burner ΔT from Flame Combustion, °F*	125	125
Burner Outlet Temperature, °F	1,000	1,000
** *Unit ΔT from Thermal Combustion, °F*	435	435
Unit Outlet Temperature, °F	1,435	1,435
Burner Duty, MM Btu/hr	—	—
Estimated Unit Removal Efficiency	—	—

* *Assumes 20% fume combustion in burner flame*

** *Assumes 95% overall fume combustion*

TABLE 74

CATALYTIC AFTERBURNER PROCESS DESCRIPTION FOR RESIN REACTOR SPECIFICATION

This specification describes the requirements for a catalytic combustion system for abatement of the hydrocarbon emissions from the resin production facility of a paint and varnish plant. The system will be similar to that shown in Figure 9. All reactor thinning tanks and product rundown tanks will be vented to the collection system. Dilution air will be supplied through a hood over the resin filter press(es). A minimum flow damper is to be supplied in this part of the ventilation system. It is to be sized to allow for a maximum fume concentration of 40% LEL in the fully closed position. A high velocity Venturi section is to be located at the afterburner inlet to assure gas flow is in excess of flame propagation velocity at 1/2 design flow rate.*

The afterburner is to be natural gas fired. Sufficient gas, having a specific gravity of 0.60 and an upper heating value of 1040 Btu/SCF, is available at a pressure of 1.0 psig.

The exhaust gas contains sufficient oxygen, greater than 16% O_2, to allow firing of the afterburner with a raw gas or process air burner. A combustion air system is not required. Fume load to the afterburner is composed of 75% kettle emission and 25% from other sources. Average emissions are 60% of peak. The system is to be designed on peak emission but operating costs are to be based on average emissions. Operating conditions listed are based on peak emissions. Fume destruction in burner is to be calculated as follows:

10% for catalytic units with or without heat exchange

10% for thermal units with heat exchange

20% for thermal units without heat exchange

Please fill in estimated efficiency of afterburner and burner duty, catalyst face velocity, and catalyst volume.

The afterburner is to be supplied with a suitable control panel and all equipment is to be designed for outdoor operation. Afterburner operating and safety controls are to be designed to meet F.I.A. (Factory Insurance Association) requirement. All dampers are to be pneumatically operated and contain an integral fail safe air reservoir. The system is to automatically divert in the event of low flow, high afterburner temperature, high reactor pressure, and afterburner preheat burner failure. The exhaust system should also be purged with inert gas on fan failure or loss of flow. Damper operating is to be sequential with the position switches mounted on the damper arm and not the operator. The system fan shall be located after the preheat burner or the afterburner outlet and shall be constructed to withstand 200°F higher than design operating temperature. The fan shall have a vee belt drive and fan and motor shall have the capacity to overcome the pressure drop of the ductwork, afterburner and any heat exchanger that may be used. System ductwork should be sized for a maximum ΔP of 2 in. w.c. hot. The fan motor may be sized for restricted flow cold start. The ductwork to the afterburner should be heated either by the use of a double manifold or hot gas recycle or a combination of both.

The heat exchanger when included is to be the parallel flow shell and tube type and designed to operate at an afterburner outlet temperature of 1200°F. Maximum exchanger pressure drop, both sides, should not exceed a total of 6 in. w.c. hot. Dirty gas is to flow through the tube side.

*Appendix B

TABLE 74 (Continued)

INSTALLATION

A complete turnkey proposal including ductwork, structural steel, fuel and inert gas piping, etc., is requested. For the purpose of this proposal fan and damper including operators are to be considered as auxiliary. The controls and control cabinet are to be included with the afterburner price. The afterburner will be assumed to be located on a structural steel base on the resin plant roof. No modification to the building structural steel is required. A tie through the roof from the base to the building steel is required. The base and tie in are part of the installed structural cost. All utilities are available within 30 ft of the control cabinet, motor, and burner. Plant air is available at 100 psig and located within 30 ft. Inert gas is available and will require 30 ft of piping from supply to ductwork. The existing stack can be used for the diversion stack. A 10 ft exhaust stack will be mounted on the afterburner, double manifold or exhaust fan. A total of thirty-five (35) feet of new exhaust ductwork and twenty-five (25) feet of double manifold will be required.

TABLE 75

CATALYTIC AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION
(Without Heat Exchange)

	Small	Large
Process Conditions		
Reactors, Number	1	2
Size each, gal	1,700	5,000
Hcbn Emission Max, lb/hr	42.4	254
Hcbn Emission Ave, lb/hr	24.7	148
Total Exhaust Rate, SCFM	1,000	6,000
Exhaust Temperature, °F	110	110
Heat of Combustion of Reactor Fume, Btu/lb	17,000	17,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Afterburner Without Heat Exchange		
Unit Inlet, °F	300	300
Burner ΔT from Fuel Gas, °F	240	240
* Burner ΔT from Flame Combustion, °F	60	60
Burner Outlet Temperature, °F	600	600
** Unit ΔT from Thermal Combustion, °F	500	500
Unit Outlet Temperature, °F	1,100	1,100
Burner Duty, MM Btu/hr	—	—
Estimated Unit Removal Efficiency	—	—
***Catalyst Face Velocity, SF/min	—	—
Catalyst Volume, ft³	—	—

* Assumes 10% fume combustion in burner flame
** Assumes 95% overall fume combustion
*** Basis 70°F exhaust temperature

TABLE 76

CATALYTIC AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION
(Without Heat Exchange)

	Small	Large
Process Conditions		
Reactors, Number	1	3
Size each, gal	5,000	5,000
Hcbn Emission Max, lb/hr	127	423
Hcbn Emission Ave, lb/hr	74	246
Total Exhaust Rate, SCFM	3,000	10,000
Exhaust Temperature, °F	110	110
Heat of Combustion of Reactor Fume, Btu/lb	17,000	17,000
Hydrocarbon Concentration		
Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Afterburner Without Heat Exchange		
Unit Inlet, °F	300	300
Burner ΔT from Fuel Gas, °F	240	240
* Burner ΔT from Flame Combustion, °F	60	60
Burner Outlet Temperature, °F	600	600
** Unit ΔT from Thermal Combustion, °F	500	500
Unit Outlet Temperature, °F	1,100	1,100
Burner Duty, MM Btu/hr	—	—
Estimated Unit Removal Efficiency	—	—
***Catalyst Face Velocity, SF/min	—	—
Catalyst Volume, ft^3	—	—

* Assumes 10% fume combustion in burner flame
** Assumes 95% overall fume combustion
*** Basis 70°F exhaust temperature

TABLE 77

CATALYTIC AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION
(With Heat Exchange)

	Small	Large
Process Conditions		
Reactors, Number		2
Size each, gal		5,000
Hcbn Emission Max, lb/hr		254
Hcbn Emission Ave, lb/hr		148
Total Exhaust Rate, SCFM		6,000
Exhaust Temperature, °F		110
Heat of Combustion of Reactor Fume, Btu/lb		17,000
Hydrocarbon Concentration Maximum, Btu/SCF		12
Average, Btu/SCF		7
Afterburner with Heat Exchange		
Inlet Tube Side, °F		300
Unit Inlet, °F		500
Burner ΔT from Fuel Gas, °F		40
* Burner ΔT from Flame Combustion, °F		60
Burner Outlet Temperature, °F		600
** Unit ΔT from Thermal Combustion, °F		500
Unit Outlet Temperature, °F		1,100
Outlet Shell Side, °F		915
Burner Duty, MM Btu/hr		—
Exchanger Duty, MM Btu/hr		—
Thermal Efficiency		~23%
Overall Heat Trans. Coef., U		—
Tube Surface Area, ft^2		—
Estimated Unit Removal Efficiency		—
***Catalyst Face Velocity, SF/min		—
Catalyst Volume, ft^3		—

* Assumes 10% fume combustion in burner flame

** Assumes 95% overall fume combustion

***Basis 70°F exhaust temperature

TABLE 78

CATALYTIC AFTERBURNER OPERATING CONDITIONS

FOR RESIN REACTOR SPECIFICATION
(With Heat Exchange)

	Small	Large
Process Conditions		
Reactors, Number	1	3
Size each, gal	5,000	5,000
Hcbn Emission Max, lb/hr	127	423
Hcbn Emission Ave, lb/hr	74	246
Total Exhaust Rate, SCFM	3,000	10,000
Exhaust Temperature, °F	110	110
Heat of Combustion of Reactor Fume, Btu/lb	17,000	17,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Afterburner with Heat Exchange		
Inlet Tube Side, °F	300	300
Unit Inlet, °F	500	500
Burner ΔT from Fuel Gas, °F	40	40
* Burner ΔT from Flame Combustion, °F	60	60
Burner Outlet Temperature, °F	600	600
** Unit ΔT from Thermal Combustion, °F	500	500
Unit Outlet Temperature, °F	1,100	1,100
Outlet Shell Side, °F	915	915
Burner Duty, MM Btu/hr	—	—
Exchanger Duty, MM Btu/hr	—	—
Thermal Efficiency	~23%	~23%
Overall Heat Trans. Coef., U	—	—
Tube Surface Area, ft^2	—	—
Estimated Unit Removal Efficiency	—	—
***Catalyst Face Velocity, SF/min	—	—
Catalyst Volume, ft^3	—	—

* Assumes 10% fume combustion in burner flame

** Assumes 95% overall fume combustion

*** Basis 70°F exhaust temperature

TABLE 79

CATALYTIC AFTERBURNER PROCESS DESCRIPTION FOR OPEN KETTLE SPECIFICATION

This specification describes the requirements for a catalytic combustion system for abatement of the hydrocarbon emissions from the resin production facility of a paint and varnish plant. The system will be similar to that shown in Figure 9. All reactor thinning tanks and product rundown tanks will be vented to the collection system. Dilution air will be supplied through a hood over the resin filter press(es). A minimum flow damper is to be supplied in this part of the ventilation system. It is to be sized to allow for a maximum fume concentration of 40% LEL in the fully closed position. A high velocity Venturi section is to be located at the afterburner inlet to assure gas flow is in excess of flame propagation velocity at 1/2 design flow rate.*

The afterburner is to be natural gas fired. Sufficient gas, having a specific gravity of 0.60 and an upper heating value of 1040 Btu/SCF, is available at a pressure of 1.0 psig.

The exhaust gas contains sufficient oxygen, greater than 16% O_2, to allow firing of the afterburner with a raw gas or process air burner. A combustion air system is not required. Fume load to the afterburner is composed of 75% kettle emission and 25% from other sources. Average emissions are 60% of peak. The system is to be designed on peak emission but operating costs are to be based on average emissions. Operating conditions listed are based on peak emissions. Fume destruction in burner is to be calculated as follows:

> *10% for catalytic units with or without heat exchange*
>
> *10% for thermal units with heat exchange*
>
> *20% for thermal units without heat exchange*
>
> *Please fill in estimated efficiency of afterburner and burner duty, catalyst face velocity, and catalyst volume.*

The afterburner is to be supplied with a suitable control panel and all equipment is to be designed for outdoor operation. Afterburner operating and safety controls are to be designed to meet F.I.A. (Factory Insurance Association) requirement. All dampers are to be pneumatically operated and contain an integral fail safe air reservoir. The system is to automatically divert in the event of low flow, high afterburner temperature, high reactor pressure, and afterburner preheat burner failure. The exhaust system should also be purged with inert gas on fan failure or loss of flow. Damper operating is to be sequential with the position switches mounted on the damper arm and not the operator. The system fan shall be located after the preheat burner or the afterburner outlet and shall be constructed to withstand 200°F higher than design operating temperature. The fan shall have a vee belt drive and fan and motor shall have the capacity to overcome the pressure drop of the ductwork, afterburner and any heat exchanger that may be used. System ductwork should be sized for a maximum ΔP of 2 in. w.c. hot. The fan motor may be sized for restricted flow cold start. The ductwork to the afterburner should be heated either by the use of a double manifold or hot gas recycle or a combination of both.

The heat exchanger when included is to be the parallel flow shell and tube type and designed to operate at an afterburner outlet temperature of 1200°F. Maximum exchanger pressure drop, both sides, should not exceed a total of 6 in. w.c. hot. Dirty gas is to flow through the tube side.

**Appendix B*

TABLE 79 (Continued)

INSTALLATION

A complete turnkey proposal including ductwork, structural steel, fuel and inert gas piping, etc., is requested. For the purpose of this proposal fan and damper including operators are to be considered as auxiliary. The controls and control cabinet are to be included with the afterburner price. The afterburner will be assumed to be located on a structural steel base on the resin plant roof. No modification to the building structural steel is required. A tie through the roof from the base to the building steel is required. The base and tie in are part of the installed structural cost. All utilities are available within 30 ft of the control cabinet, motor, and burner. Plant air is available at 100 psig and located within 30 ft. Inert gas is available and will require 30 ft of piping from supply to ductwork. The existing stack can be used for the diversion stack. A 10 ft exhaust stack will be mounted on the afterburner, double manifold or exhaust fan. A total of thirty-five (35) feet of new exhaust ductwork and twenty-five (25) feet of double manifold will be required.

TABLE 80

CATALYTIC AFTERBURNER OPERATING CONDITIONS

FOR OPEN KETTLE SPECIFICATION
(Without Heat Exchange)

	Small	Large
Process Conditions		
Kettles, Number	1	6
Size each, gal	300	300
Hcbn Emission Max, lb/hr	22.5	135
Hcbn Emission Ave, lb/hr	13.1	78.8
Total Exhaust Rate, SCFM	500	3,000
Exhaust Temperature, °F	80	80
Heat of Combustion of Kettle Fume, Btu/lb	16,000	16,000
Hydrocarbon Concentration		
Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Afterburner Without Heat Exchange		
Unit Inlet, °F	280	280
Burner ΔT from Fuel Gas, °F	260	260
* *Burner ΔT from Flame Combustion, °F*	60	60
Burner Outlet Temperature, °F	600	600
** *Unit ΔT from Thermal Combustion, °F*	500	500
Unit Outlet Temperature, °F	1,100	1,100
Burner Duty, MM Btu/hr	—	—
Estimated Unit Removal Efficiency	—	—
*** *Catalyst Face Velocity, SF/min*	—	—
Catalyst Volume, ft³	—	—

* *Assumes 10% fume combustion in burner flame*
** *Assumes 95% overall fume combustion*
*** *Basis 70°F exhaust temperature*

TABLE 81

CATALYTIC AFTERBURNER OPERATING CONDITIONS

FOR OPEN KETTLE SPECIFICATION
(Without Heat Exchange)

	Small	Large
Process Conditions		
Kettles, Number	2	4
Size each, gal	300	300
Hcbn Emission Max, lb/hr	45	90
Hcbn Emission Ave, lb/hr	262	52
Total Exhaust Rate, SCFM	1,000	2,000
Exhaust Temperature, °F	80	80
Heat of Combustion of Kettle Fume, Btu/lb	16,000	16,000
Hydrocarbon Concentration Maximum, Btu/SCF	12	12
Average, Btu/SCF	7	7
Afterburner Without Heat Exchange		
Unit Inlet, °F	280	280
Burner ΔT from Fuel Gas, °F	260	260
* Burner ΔT from Flame Combustion, °F	60	60
Burner Outlet Temperature, °F	600	600
** Unit ΔT from Thermal Combustion, °F	500	500
Unit Outlet Temperature, °F	1,100	1,100
Burner Duty, MM Btu/hr	—	—
Estimated Unit Removal Efficiency	—	—
***Catalyst Face Velocity, SF/min	—	—
Catalyst Volume, ft^3	—	—

* Assumes 10% fume combustion in burner flame
** Assumes 95% overall fume combustion
*** Basis 70°F exhaust temperature

TABLE 82

CITY COST INDICES

Average 1969 Construction Cost & Labor Indices						Historical Average	
	Index			Index		Year	Index
City	Labor	Total	City	Labor	Total	1969	100
Albany, N.Y.	98	100	Milwaukee, Wi.	103	108	1968	91
Albuquerque, N.M.	86	95	Minneapolis, Mn.	99	98	1967	86
Amarillo, Tx.	87	84	Mobile, Al.	94	90	1966	83
Anchorage, Ak.	131	148	Montreal, Can.	77	89	1965	79
Atlanta, Ga.	88	94	Nashville, Tn.	79	82	1964	78
Baltimore, Md.	90	93	Newark, N.J.	122	109	1963	76
Baton Rouge, La.	83	88	New Haven, Ct.	102	100	1962	74
Birmingham, Al.	79	86	New Orleans, La.	89	95	1961	72
Boston, Ma.	106	103	New York, N.Y.	132	118	1960	71
Bridgeport, Ct.	104	102	Norfolk, Va.	73	77	1959	69
Buffalo, N.Y.	104	107	Oklahoma City, Ok.	82	88	1958	67
Burlington, Vt.	86	90	Omaha, Nb.	90	93	1957	65
Charlotte, N.C.	70	75	Philadelphia, Pa.	106	101	1956	63
Chattanooga, Tn.	81	84	Phoenix, Az.	101	97	1955	59
Chicago, Ill.	107	103	Pittsburgh, Pa.	110	106	1954	58
Cincinnati, Oh.	108	104	Portland, Me.	82	87	1953	57
Cleveland, Oh.	121	112	Portland, Or.	102	103	1952	55
Columbus, Oh.	106	99	Providence, R.I.	98	97	1951	53
Dallas, Tx.	86	89	Richmond, Va.	76	79	1950	49
Dayton, Oh.	100	103	Rochester, N.Y.	110	107	1949	48
Denver, Co.	94	91	Rockford, Ill.	109	109	1948	48
Des Moines, Ia.	93	96	Sacramento, Ca.	117	110	1947	43
Detroit, Mi.	117	111	St. Louis, Mo.	110	103	1946	35
Edmonton, Cn.	80	83	Salt Lake City, Ut.	93	95	1945	30
El Paso, Tx.	77	83	San Antonio, Tx.	82	82	1944	29
Erie, Pa.	98	99	San Diego, Ca.	111	107	1943	29
Evansville, In.	93	97	San Francisco, Ca.	124	109	1942	28
Grand Rapids, Mi.	103	99	Savannah, Ga.	72	77	1941	25
Harrisburg, Pa.	90	92	Scranton, Pa.	94	96	1940	24
Hartford, Ct.	104	100	Seattle, Wa.	104	99	1939	23
Honolulu, Hi.	99	109	Shreveport, La.	82	89	1938	23
Houston, Tx.	92	89	South Bend, In.	99	97	1937	23
Indianapolis, In.	97	98	Spokane, Wa.	101	100	1936	20
Jackson, Ms.	73	75	Springfield, Ma.	99	97	1935	20
Jacksonville, Fl.	78	79	Syracuse, N.Y.	105	103	1934	20
Kansas City, Mo.	94	93	Tampa, Fl.	81	84	1933	18
Knoxville, Tn.	82	82	Toledo, Oh.	105	105	1932	17
Las Vegas, Nv.	115	107	Toronto, Cn.	84	93	1931	20
Little Rock, Ar.	78	81	Trenton, N.J.	114	103	1930	22
Los Angeles, Ca.	113	102	Tulsa, Ok.	85	89	1929	23
Louisville, Ky.	92	93	Vancouver, Cn.	81	91	1928	23
Madison, Wi.	95	98	Washington, D.C.	98	94	1927	23
Manchester, N.H.	89	92	Wichita, Ks.	85	90	1926	23
Memphis, Tn.	83	82	Winnipeg, Cn.	62	82	1925	23
Miami, Fl.	98	94	Youngstown, Oh.	107	106	1924	23

TABLE 83

AVERAGE HOURLY LABOR RATES BY TRADE

Trade	1970	1969	1968	1967	1966
Common Building Labor	$5.00	$4.55	$4.10	$3.85	$3.65
Skilled Average	6.85	6.05	5.50	5.15	4.90
Helpers Average	5.15	4.65	4.20	4.00	3.85
Foremen (usually 35¢ over trade)	7.20	6.40	5.85	5.50	5.25
Bricklayers	7.15	6.40	5.85	5.55	5.35
Bricklayers Helpers	5.20	4.70	4.30	4.05	3.95
Carpenters	6.95	6.15	5.40	5.10	4.90
Cement Finishers	6.75	5.90	5.30	5.05	4.85
Electricians	7.50	6.45	5.95	5.60	5.45
Glaziers	6.25	5.50	5.10	4.75	4.60
Hoist Engineers	7.05	5.90	5.40	5.10	4.85
Lathers	6.60	5.95	5.45	5.20	5.05
Marble & Terrazzo Workers	6.45	5.60	5.25	5.05	4.90
Painters, Ordinary	6.20	5.45	5.05	4.75	4.50
Painters, Structural Steel	6.50	5.80	5.30	4.95	4.80
Paperhangers	6.30	5.60	5.15	4.75	4.55
Plasterers	6.60	5.95	5.50	5.15	5.00
Plasterers Helpers	5.30	4.85	4.45	4.15	4.00
Plumbers	7.75	6.90	6.15	5.75	5.55
Power Shovel or Crane Operator	7.20	6.20	5.65	5.35	5.05
Rodmen (Reinforcing)	7.30	6.35	5.80	5.45	5.15
Roofers, Composition	6.30	5.55	5.05	4.75	4.65
Roofers, Tile & Slate	6.35	5.60	5.10	4.85	4.80
Roofers Helpers (Composition)	4.75	4.45	4.00	3.75	3.55
Steamfitters	7.70	6.90	6.10	5.70	5.50
Sprinkler Installers	7.70	6.90	6.10	5.70	5.50
Structural Steel Workers	7.45	6.45	5.90	5.55	5.25
Tile Layers (Floor)	6.50	5.60	5.20	4.90	4.80
Tile Layers Helpers	5.25	4.80	4.35	4.15	4.05
Truck Drivers	5.15	4.60	4.30	3.95	3.65
Welders, Structural Steel	7.15	6.35	5.80	5.45	5.10

TABLE 84

INSTALLATION AND OPERATING COST FOR BAGHOUSE

Type Collector	Type Pulse	Shaker
Bag type	Polyester felt	Cotton sateen
Cloth, ft^2	452	1,900
Air, CFM	3,800	3,800
Air/cloth ratio CFM/ft^2	8.4/1	2/1
Capital cost, $	3,900	4,500
Installation cost, $	2,900	3,400
Total cost, $	6,800	7,900
Operating & Maintenance Cost - 8 hr day, $	350/yr	245/yr
Pigment recovered, lb/yr	2,850	2,850
Compressed air required @ 100 psig	4.5 SCFM Ave. 9.0 SCFM Max.	None

FIGURE 64

CAPITAL COSTS
FOR
CATALYTIC AFTERBURNERS
WITHOUT HEAT EXCHANGE

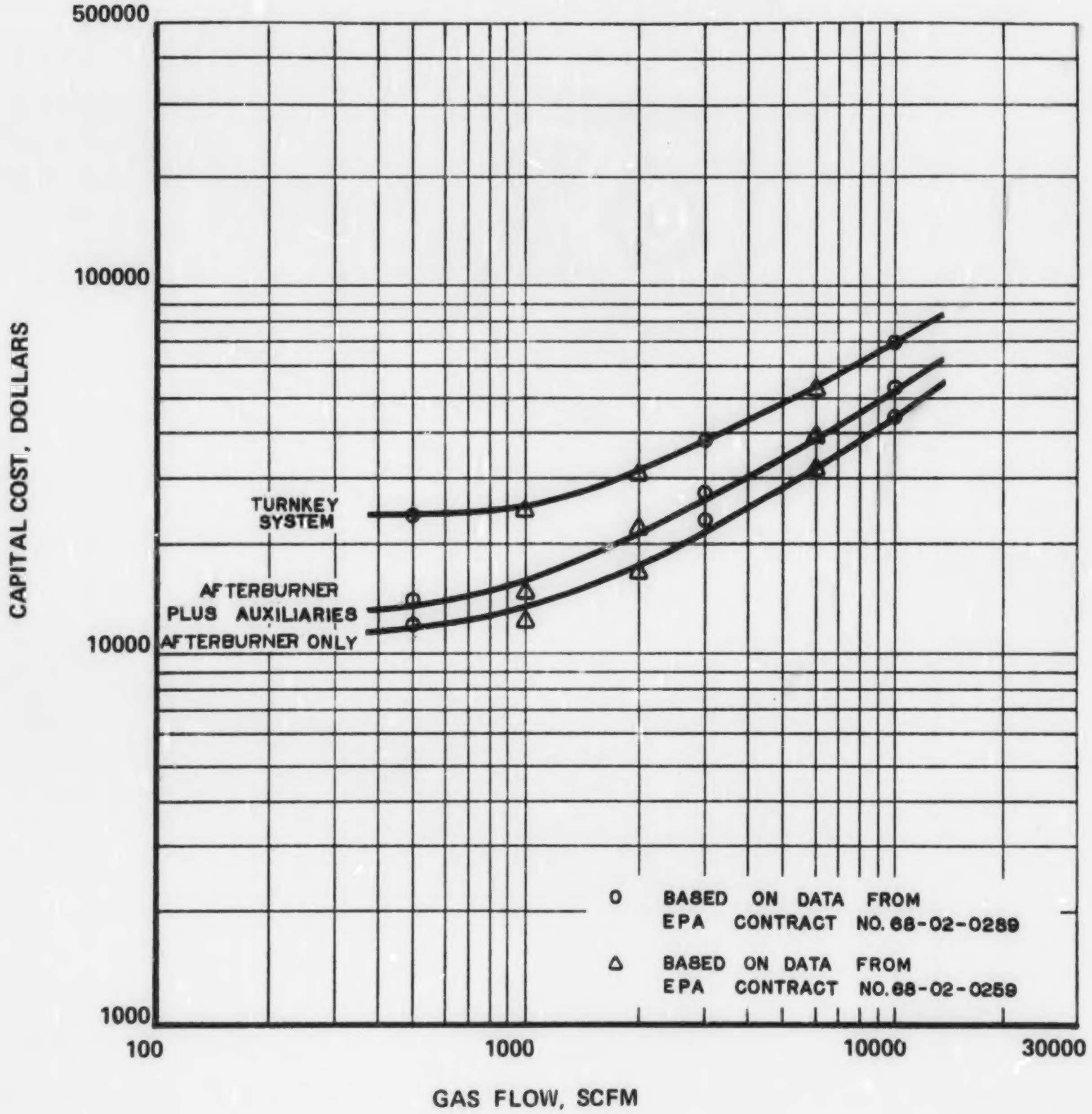


FIGURE 65

CAPITAL COSTS FOR CATALYTIC AFTERBURNERS WITH (23% EFFICIENT) HEAT EXCHANGE

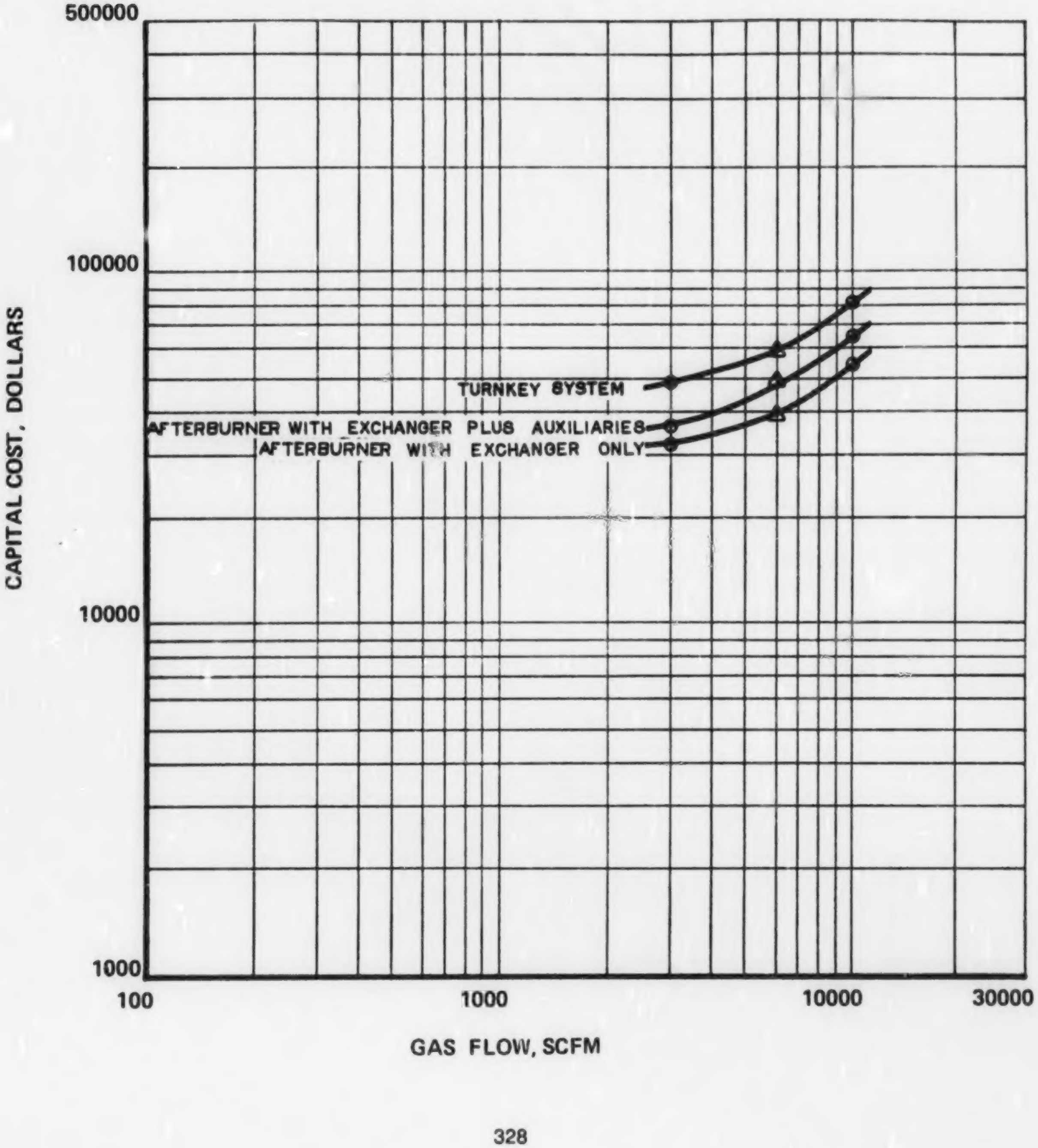


FIGURE 66

CAPITAL COSTS
FOR
THERMAL AFTERBURNERS
WITHOUT HEAT EXCHANGE

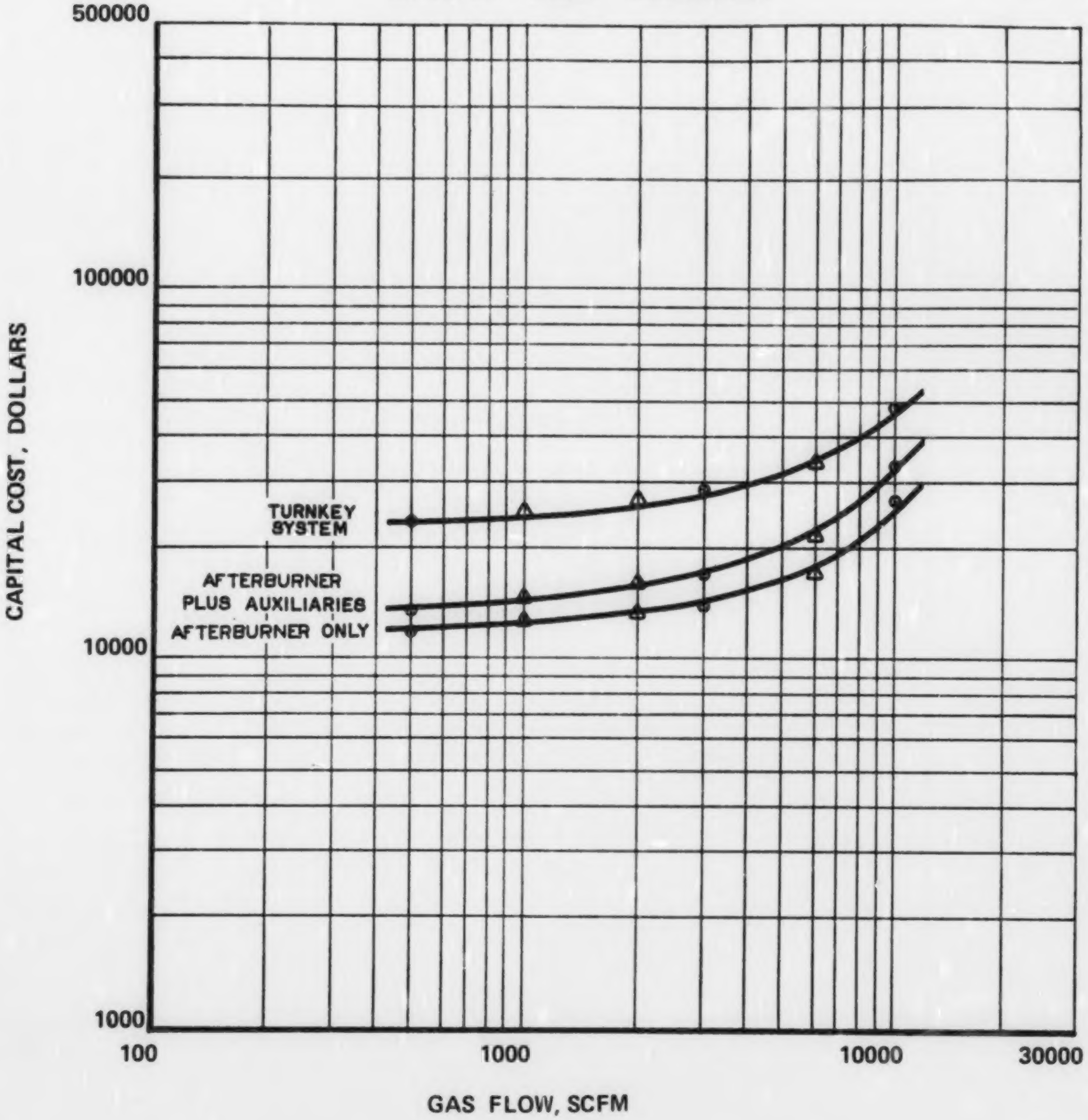


FIGURE 67

CAPITAL COSTS FOR THERMAL AFTERBURNER WITH (42% EFFICIENT) HEAT EXCHANGE

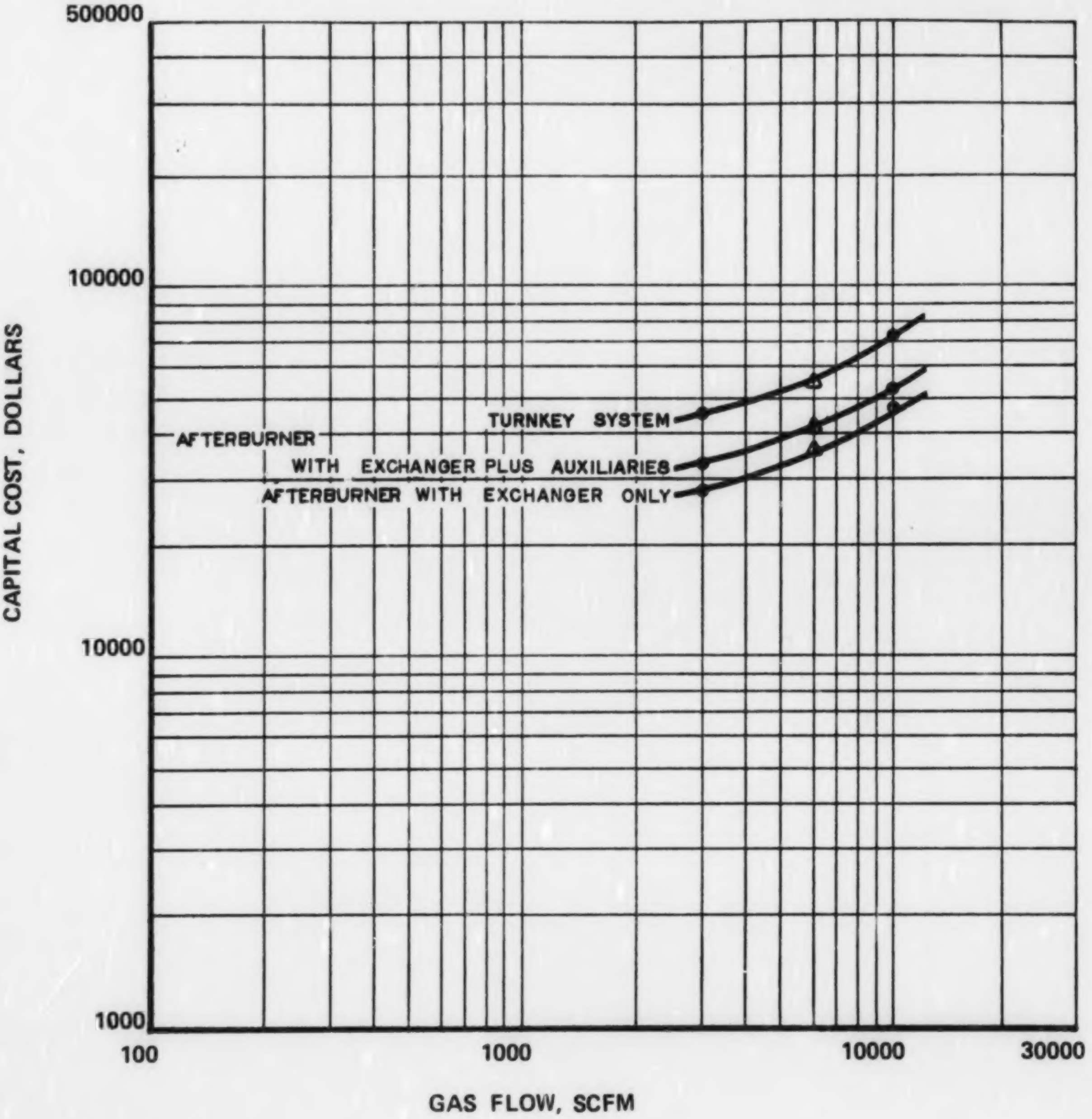


FIGURE 68

TOTAL INSTALLED COSTS FOR THERMAL AND CATALYTIC AFTERBURNERS

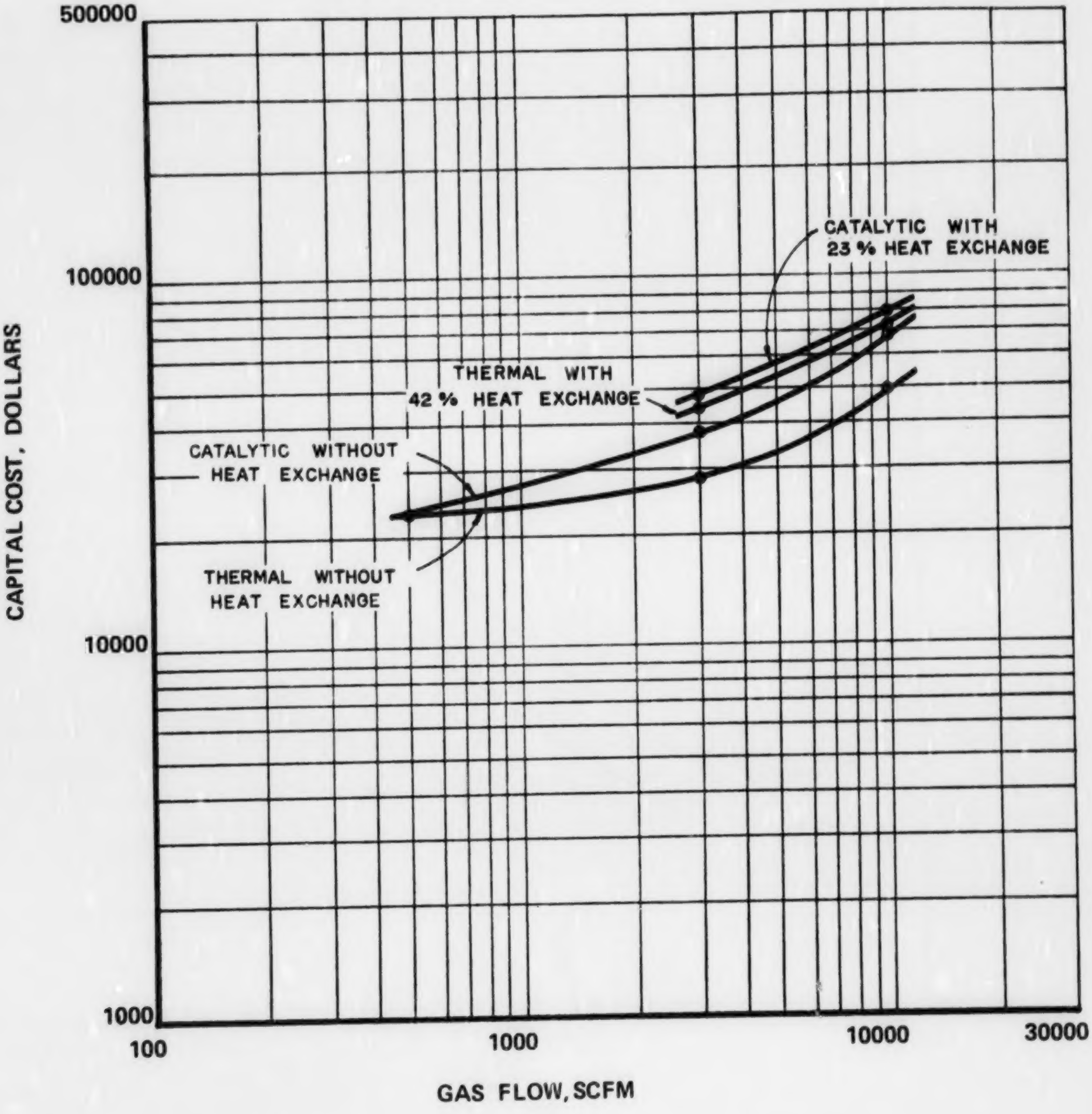


FIGURE 69

DIRECT ANNUAL OPERATING COSTS
FOR
THERMAL AND CATALYTIC AFTERBURNERS
WITHOUT HEAT EXCHANGE

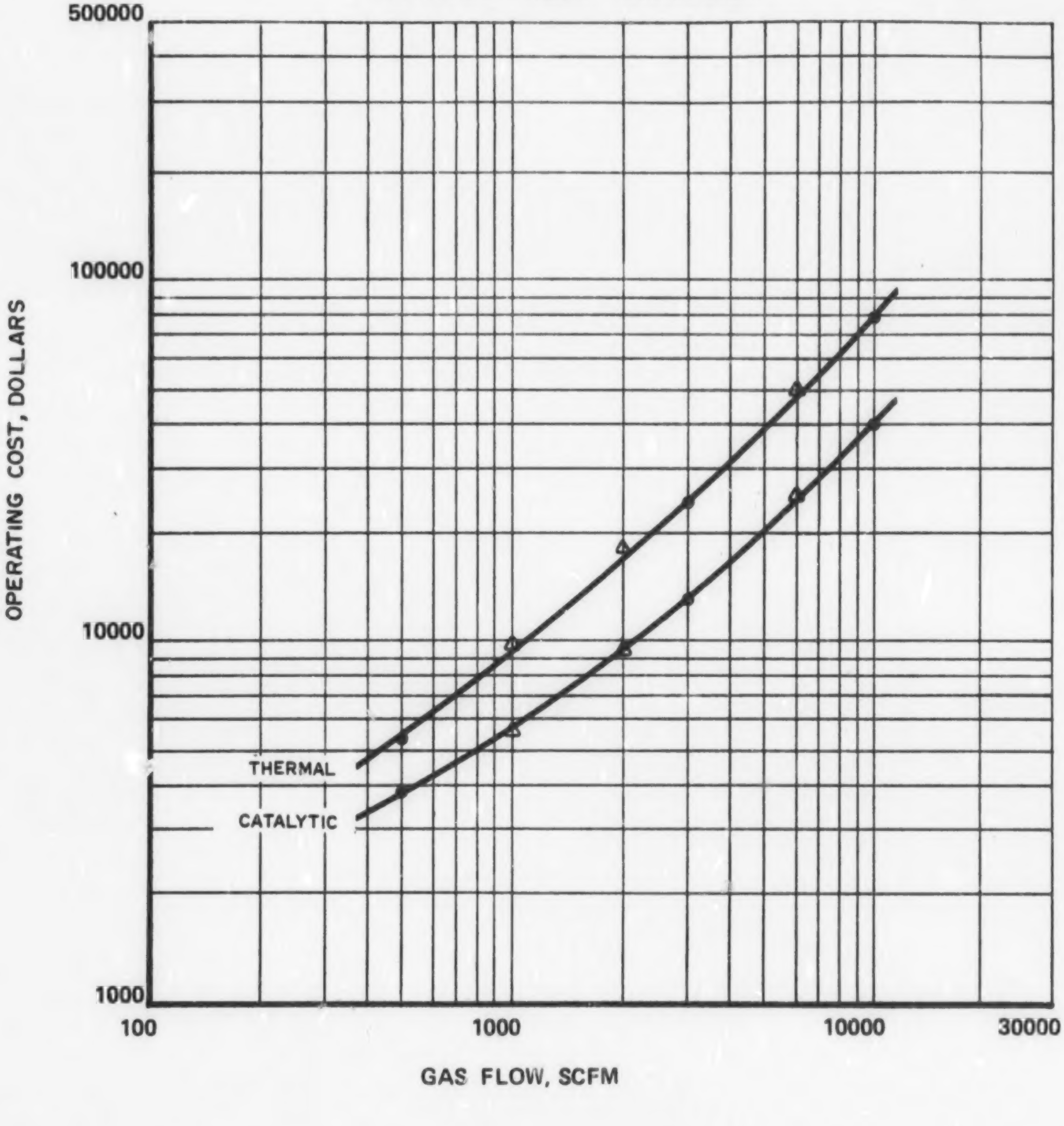


FIGURE 70

TOTAL ANNUAL OPERATING COST
FOR
THERMAL AND CATALYTIC AFTERBURNERS WITHOUT HEAT EXCHANGE

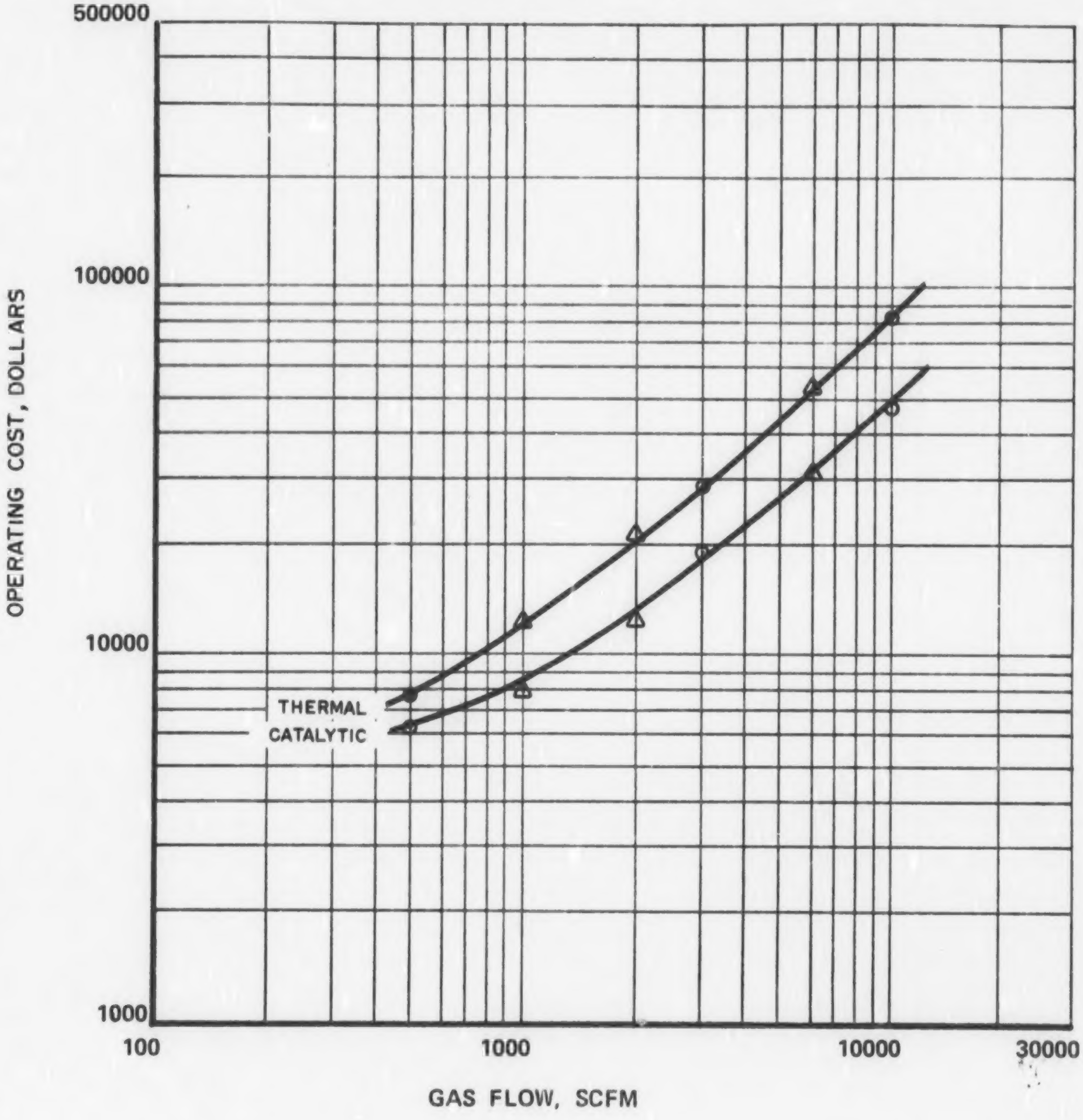


FIGURE 71

DIRECT ANNUAL OPERATING COST
FOR
THERMAL AND CATALYTIC AFTERBURNERS WITH HEAT EXCHANGE

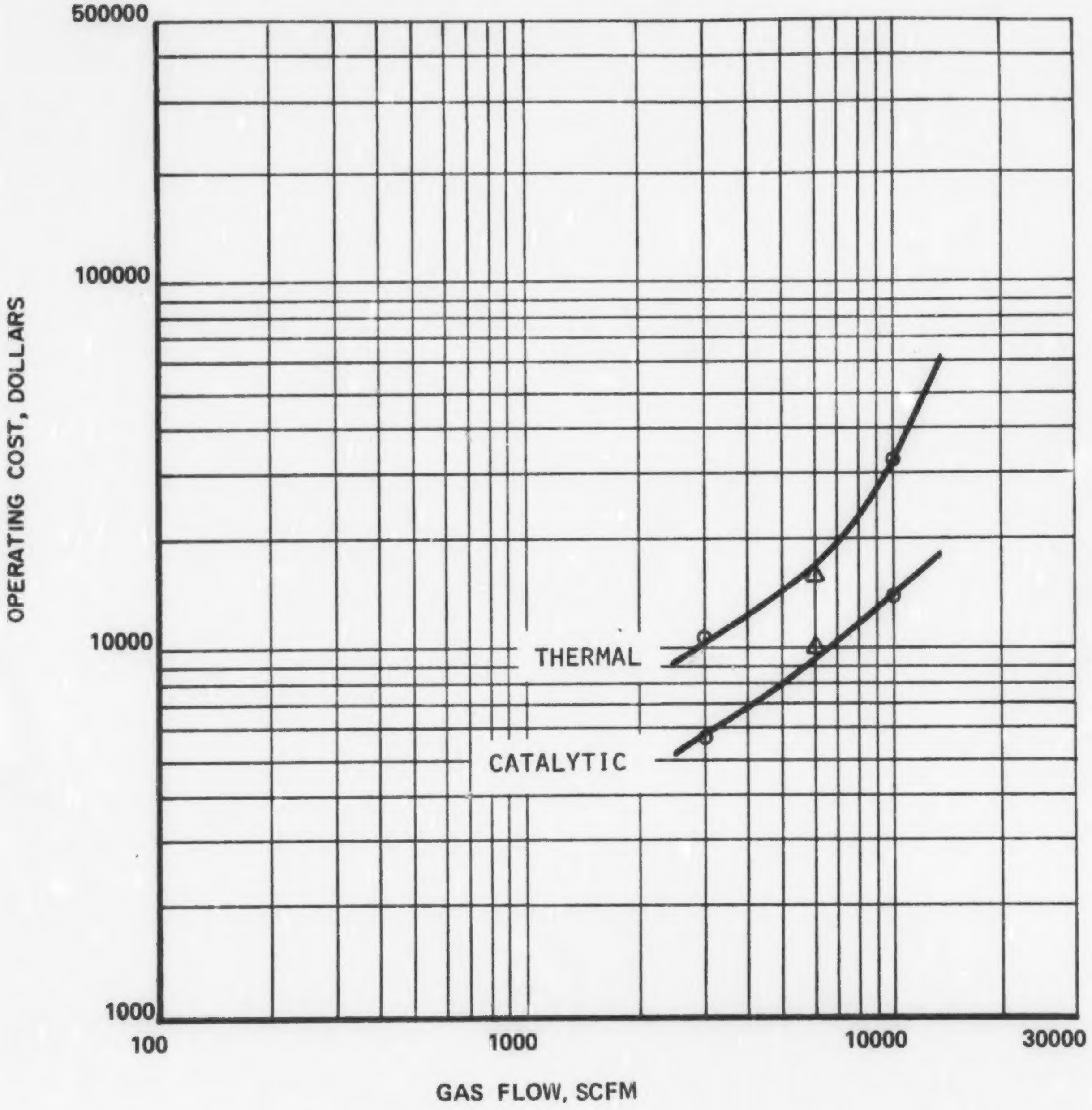


FIGURE 72

TOTAL ANNUAL OPERATING COST
FOR
THERMAL AND CATALYTIC AFTERBURNERS WITH HEAT EXCHANGE

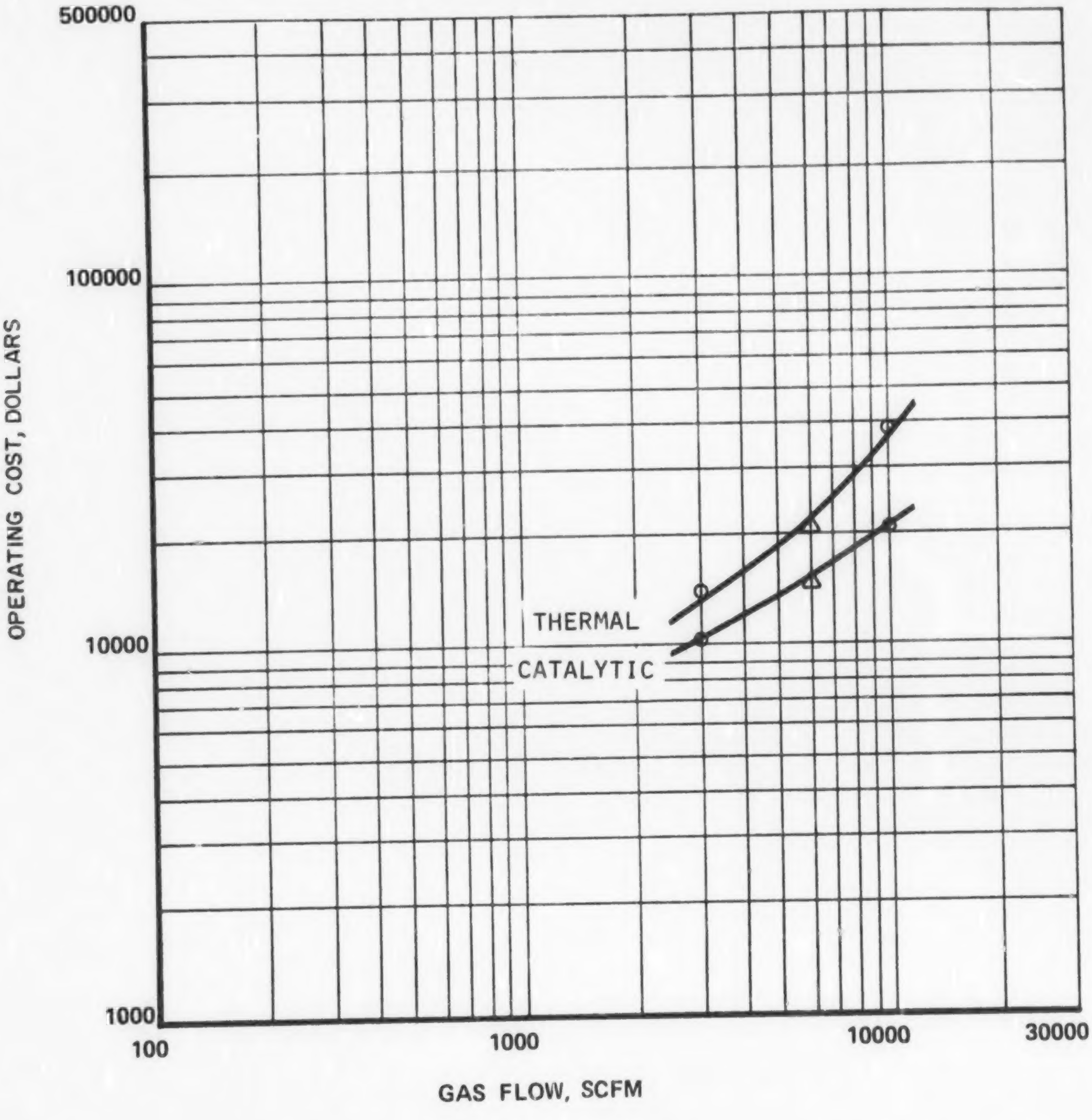


TABLE 85

MODEL PLANT ANNUAL RAW MATERIAL COSTS

(FINISHED OUTPUT OF 1.9 MILLION GALLONS)

Raw Material	Trade Sales Products				Industrial Finishes Products				
	Pounds	Gallons	Price Dlvd. (Per 100)	Value	Pounds	Gallons	Price Dlvd. (Per 100)	Value	Total
Pigments & Extenders									
Titanium Dioxide	2,039,000	–	$27.00	$550,530.00	760,000	–	$27.00	$205,200.00	$775,730.00
Misc. Colors	27,500	–	46.50	12,787.50	380,000	–	46.50	176,700.00	189,487.50
Silica	1,179,000	–	2.05	24,169.50	232,750	–	2.05	4,771.38	28,940.88
Calcium Carbonate	893,500	–	2.79	24,928.65	–	–	–	–	24,928.65
Talc	475,850	–	3.32	15,798.22	522,500	–	3.32	17,347.00	33,145.22
Clay	199,700	–	3.18	6,350.46	–	–	–	–	6,350.46
Total Pigments & Extenders				$634,564.33				$404,018.38	$1,038,582.71
Resins – Manufactured									
Soya Oil	714,000	–	$11.35	$ 81,039.00	492,000	–	$11.35	$ 55,842.00	$136,881.00
Phthalic Anhydride	276,000	–	9.80	27,048.00	470,000	–	9.80	46,060.00	73,108.00
Glycerine	138,000	–	23.00	17,940.00	247,000	–	23.00	56,810.00	74,750.00
Total Manufactured Resins				$126,027.00				$158,712.00	$284,759.00
Resins – Purchased									
Exterior Latex (11.42 lb/gal)	1,644,500	–	$16.25	$267,231.25	–	–	–	–	$267,231.25
Interior Latex (10.6 lb/gal)	2,141,200	–	15.75	337,239.00	–	–	–	–	337,239.00
Aropol 830-V-60®	–	–	–	–	400,000	–	24.70	98,800.00	98,800.00
Aroplaz 7435-XM-50®	–	–	–	–	870,000	–	22.95	199,665.00	199,665.00
Resimene V-920®	–	–	–	–	152,000	–	20.75	31,540.00	31,540.00
Acryloid AT-51®	–	–	–	–	510,000	–	30.50	155,550.00	155,550.00
Epon 1001X75®	–	–	–	–	60,600	–	36.50	22,119.00	22,119.00
Total Purchased Resins				$604,470.25				$507,674.00	$1,112,144.25

TABLE 85 (continued)

Raw Material	Trade Sales Products				Industrial Finishes Products				
	Pounds	Gallons	Price Dlvd. (Per 100)	Value	Pounds	Gallons	Price Dlvd. (Per 100)	Value	Total
Solvents & Miscellaneous									
Driers (9.8 lb/gal)	55,890	–	$27.00	$ 15,090.30	81,340	–	$27.00	$ 21,961.80	$ 37,052.10
Misc. Solids	29,200	–	40.00	11,680.00	–	–	–	–	11,680.00
Misc. Liquids (8 lb/gal)	241,600	–	40.00	96,640.00	30,400	–	40.00	12,160.00	108,800.00
Water	–	272,300	.03	81.69	–	–	–	–	81.69
Odorless Mineral Spirits	–	169,500	30.00	50,850.00	–	–	–	–	50,850.00
Anti-Skin (7.72 lb/gal)	26,402	–	41.00	10,824.82	22,774	–	41.00	9,337.34	20,162.16
Toluene	–	–	–	–	–	45,600	23.00	10,488.00	10,488.00
Xylene	–	–	–	–	–	221,400	24.00	53,136.00	53,136.00
Aromatic 100 (Solvesso 100)	–	–	–	–	–	20,900	26.00	5,434.00	5,434.00
Aromatic 150 (Solvesso 150)	–	–	–	–	–	6,975	27.50	1,918.13	1,918.13
VM + P Naphtha	–	–	–	–	–	32,650	18.50	6,040.25	6,040.25
Butanol (6.74 lb/gal)	–	–	–	–	20,894	–	8.75	1,828.23	1,828.23
Cellosolve Acetate	–	–	–	–	67,300	–	15.00	10,095.00	10,095.00
Triethyl Amine (6.07 lb/gal)	–	–	–	–	577	–	42.00	242.34	242.34
Total Solvents & Miscellaneous				$185,166.81				$132,641.09	$317,807.90
Grand Total				$1,550,228.39				$1,203,045.47	$2,753,273.86

TABLE 86

MODEL PLANT ANNUAL PACKAGE & PACKAGE MATERIAL COSTS

(FINISHED OUTPUT OF 1.9 MILLION GALLONS)

	Trade Sales Products			Industrial Finishes Products		
Package Type	Quantity	Price Dlvd.	Value	Quantity	Price Dlvd.	Value
Packages						
Drums (55 gal)	–	–	–	10,364	$ 10.35/@	$107,267.40
Pails (5 gal)	22,800	$121.45/C	$ 27,690.60	12,350	121.45/C	14,999.08
Pails (5 gal) (Interior Coated)	–	–	–	25,650	136.45/C	34,999.43
Cans (gal)	273,600	286.00/M	78,249.60	–	–	–
Cans (gal) (Interior Coated)	638,400	294.50/M	188,008.80	–	–	–
Cans (qt)	205,200	118.70/M	24,357.24	–	–	–
Cans (qt) (Interior Coated)	205,200	127.20/M	26,101.44	–	–	–
Cans (pt)	91,200	88.40/M	8,062.08	–	–	–
Total Packages			$352,469.76			$157,265.91
Labels						
5 Gallon Size	22,800	9.40/M	214.32	38,000	9.40/M	357.20
Gallon Size	912,000	8.75/M	7,980.00	–	–	–
Quart Size	410,400	8.00/M	3,283.20	–	–	–
Pint Size	91,200	7.50/M	684.00	–	–	–
Total Labels			$ 12,161.52			$ 357.20
Cartons						
Gallon Size (4 gal)	228,000	145.00/M	33,060.00	–	–	–
Quart Size (6 qt)	68,400	78.00/M	5,335.20	–	–	–
Pint Size (12 pt)	7,600	94.00/M	714.40	–	–	–
Total Cartons			$ 39,109.60			–
Pallets (30 in. x 42 in. Size)						
Drums	–	–	–	5,182	3.60/@	18,655.20
5 gal Pails	1,425	3.60/@	5,130.00	2,375	3.60/@	8,550.00
Gallons	9,500	3.60/@	34,200.00	–	–	–
Quarts	977	3.60/@	3,517.20	–	–	–
Pints	136	3.60/@	489.60	–	–	–
Total Pallets			$ 43,336.80			$ 27,205.20
Grand Total Package Cost			$447,077.68			$184,828.31

TABLE 87

MODEL PLANT ANNUAL WAGE & SALARY COST OF PLANT

(FINISHED OUTPUT OF 1.9 MILLION GALLONS)

No. People	Job Title	Monthly Salary Estimate	Trade Sales Products				Industrial Finishes Products				Total Wages Salaries
			Annual Hours	Hourly Rate	Salary Alloc.	Annual Wages	Annual Hours	Hourly Rate	Salary Alloc.	Annual Wages	
Salaried											
A 1	Plant Manager	$ 1,500	–	–	$10,800	–	–	–	$ 7,200	–	$18,000
A 1	Secretary	650	–	–	4,680	–	–	–	3,120	–	7,800
A 1	Supervisor - 1st Shift	1,000	–	–	7,200	–	–	–	4,800	–	12,000
A 1	Supervisor - 2nd Shift	1,000	–	–	7,200	–	–	–	4,800	–	12,000
A 1	Supervisor Warehouse & Shipping	1,000	–	–	7,200	–	–	–	4,800	–	12,000
A 1	Quality Control Chemist	1,200	–	–	8,640	–	–	–	5,760	–	14,400
A 2	Quality Control Technicial	800	–	–	11,520	–	–	–	7,680	–	19,200
A 3	Clerks - 1st Shift	550	–	–	11,880	–	–	–	7,920	–	19,800
A 1	Clerk - 2nd Shift	575	–	–	4,140	–	–	–	2,760	–	6,900
Total Salaries					$73,260				$48,840		$122,100
Hourly Paid Employees											
1st Shift Workers											
B 15	Various Classifications	–	18,720	4.04	–	$75,629	12,480	4.04	–	$50,419	$126,048
C 2	Resin Plant Operators	–	3,328	4.04	–	13,445	832	4.04	–	3,361	16,806
2	Fillers - Industrial	–	–	–	–	–	4,160	4.04	–	16,806	16,806
2	Fillers - Trade	–	4,160	4.04	–	16,806	–	–	–	–	16,806
2	Caser & Palletizer	–	4,160	4.04	–	16,806	–	–	–	–	16,806
D 12	Stockman	–	18,720	4.04	–	75,629	6,240	4.04	–	25,210	100,839
2nd Shift Workers											
E 10	Various Classifications	–	12,480	4.14	–	51,667	8,320	4.14	–	34,445	86,112
C 2	Resin Plant Operators	–	3,328	4.14	–	13,778	832	4.14	–	3,444	17,222
2	Fillers - Industrial	–	–	–	–	–	4,160	4.14	–	17,222	17,222
2	Fillers - Trade	–	4,160	4.14	–	17,222	–	–	–	–	17,222
2	Caser & Palletizer	–	4,160	4.14	–	17,222	–	–	–	–	17,222
D 5	Stockman	–	7,800	4.14	–	32,292	2,600	4.14	–	10,764	43,056
Total Hourly Paid Wages						$330,496				$161,671	$492,167
Grand Total Wages & Salaries					$73,260	$330,496			$48,840	$161,671	$614,267

TABLE 87 (Continued)

	Trade Sales Products				Industrial Finishes Products				Total
	Annual Hours	Hourly Rate	Salary Alloc.	Annual Wages	Annual Hours	Hourly Rate	Salary Alloc.	Annual Wages	Wages - Salaries
Employer Soc. Sec. Cost (5.85% up to $10,800 Annual Wage)			$ 3,773	$19,334			$ 2,515	$ 9,458	$35,080
Other Employer Costs (Fringes) Estimated 5%			3,663	16,525			2,442	8,084	30,714
Total Employee Costs			$80,696	$366,355			$53,797	$179,213	$680,061

(A) Allocated between Trade & Industrial Products on 60% to 40% basis

(B) Allocated between Trade & Industrial Products on 60% to 40% basis: (Adjuster & Shader (1), Mill Operator (4), Mixers (3), Receiving (3), Miscellaneous (1), Maintenance (3))

(C) Allocated between Trade & Industrial Products on 80% to 20% basis: (Most Industrial Resins are purchased)

(D) Allocated between Trade & Industrial Products on 75% to 25% basis: (Industrial Output accounts for 40% but requires less handling due to larger packages)

(E) Same as (B) above except no Receiving workers on this shift and only one Maintenance employee.

NOTE: Hourly Wage Rate calculated by taking the average hourly rate of $3.68 from the statistical abstract of the U.S.-1972 plus 10% – Second Shift Rate includes another 10¢/hour for shift differential.

TABLE 88

MODEL PLANT
DEPRECIATION SCHEDULE
(Finished Output 1.9 Million Gallons)

	Asset Capitalized Value	Straight Line Depr. %	Annual Depr. Amount
LAND	$ 100,000	—	—
BUILDING & SITE PREPARATION:			
Raw Material Warehouse	219,700	1.25	$ 2,746
Manufacturing Building	912,450	1.25	11,406
Finished Goods Warehouse	526,700	1.25	6,584
Site Preparation	167,100	1.25	2,089
Engineering	217,200	1.25	2,715
Other Building Costs	310,300	1.25	2,879
Total Buildings, Etc.	$2,353,450		$ 29,419
EQUIPMENT & UTILITIES:			
Paint Plant	$ 521,900	10.00	$ 52,190
Resin Plant	222,500	10.00	22,250
Storage	211,600	10.00	21,160
Miscellaneous	142,750	10.00	14,275
Utilities	178,400	10.00	17,840
Total Equipment & Utilities	$1,277,150		$ 127,715
GRAND TOTAL	$3,730,600		$ 157,134

Note:

1. All freight & sales tax was assumed to be expensed in prior year.
2. Assumption is that plant is operating and on stream: All start-up costs have expired in prior years.
3. Depreciation will be allocated between trade and industrial products on 60% to 40% basis.

Trade	60%	$ 94,280
Industrial	40%	62,854
		$157,134

TABLE 89

MODEL PLANT
INCOME STATEMENT
(Year Ending December 31, 19–2)

	Trade Sales Products	Industrial Sales Products	Total All
REVENUE (NET)			
A) 1,140,000 gal @ $3.78/gal	$4,309,200	—	$4,309,200
A) 760,000 gal @ $3.02/gal	—	$2,295,200	2,295,200
Total Revenue	$4,309,200	$2,295,200	$6,604,400
COST OF GOODS SOLD			
Raw Materials (See Table 85)	$1,550,228	$1,203,045	$2,753,273
Packaging (See Table 86)	447,078	184,828	631,906
Salaries & Wages (See Table 87)	447,051	233,010	680,061
Depreciation (See Table 88)	94,280	62,854	157,134
B) Other Manufacturing Costs			
Trade-Estimated @ 50¢/gal	570,000	—	570,000
Industrial-Estimated @ 30¢/gal	—	228,000	228,000
Total Cost of Goods Sold	$3,108,637	$1,911,737	$5,020,374
Gross Profit	$1,200,563	$ 383,463	$1,584,026
SELLING, GENERAL & ADMINISTRATIVE EXPENSES			
Trade-Estimated @ 15% of Sales	$ 646,380	—	$ 646,380
Industrial-Estimated @ 5% of Sales	—	$ 114,761	114,761
Total S, G & A Expense	$ 646,380	$ 114,761	$ 761,141
Operating Income	$ 554,183	$ 268,702	$ 822,885
INTEREST EXPENSE			
Long-Term Debt	$ 151,200	$ 100,800	$ 252,000
Income Before Taxes	$ 402,983	$ 167,902	$ 570,885
INCOME TAXES			
Federal Income Tax (50%)	$ 201,492	$ 83,951	$ 285,443
State & Local Taxes (10%)	$ 40,298	$ 16,790	$ 57,088
Total Taxes	$ 241,790	$ 100,741	$ 342,531
NET INCOME	$ 161,193	$ 67,161	228,354

TABLE 89
(Continued)

MODEL PLANT
INCOME STATEMENT
(Year Ending December 31, 19–2)

Notes:

A) Selling price calculated as follows using data from current industrial reports, M28F - - year 1971.

TRADE -$1,563 million divided by 431 million gal = $3.63/gal
$3.63/gal times growth rate of 4% = $3.78/gal

INDUSTRIAL -$1,268 million divided by 443 million gal = $2.86/gal
$2.68/gal times growth rate of 5.5% = $3.02/gal

B) The estimated other manufacturing costs is to cover such items as:

1. Repair parts which are expensed
2. Operating, heating and utility costs
3. Property insurance and taxes
4. Miscellaneous operating expenses

TABLE 90

MODEL PLANT PRODUCTION SCHEDULE
1.9 MILLION GALLONS OUTPUT
(SAFETY STOCK 5% OF ANNUAL SHIPMENTS)

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Total
Latex House Paint													
Shipments – Gallons	9,885	14,030	14,445	32,375	28,035	50,495	39,090	26,735	25,245	10,785	9,745	12,735	273,600
Production – Gallons	22,800	22,800	22,800	22,800	22,800	22,800	22,800	22,800	22,800	22,800	22,800	22,800	273,600
Inventory Balance – Cumulative	48,050	56,820	65,175	55,600	50,365	22,670	6,380	2,445	–	12,015	25,070	35,135	31,644 Avg.
Total Inv. (incl. 13,680 gal S.S.)	61,730	70,500	78,855	69,280	64,045	36,350	20,060	16,125	13,680	25,695	38,750	48,815	45,324 Avg.
Alkyd Trim Enamel													
Shipments – Gallons	590	810	850	1,875	1,625	2,920	2,270	1,550	1,465	630	570	745	15,900
Production – Gallons	1,325	1,325	1,325	1,325	1,325	1,325	1,325	1,325	1,325	1,325	1,325	1,325	15,900
Inv. gal (Cumulative)	2,765	3,280	3,755	3,205	2,905	1,310	365	140	–	695	1,450	2,030	1,825 Avg.
Total Inv. (incl. 795 gal S.S.)	3,560	4,075	4,550	4,000	3,700	2,105	1,160	935	795	1,490	2,245	2,825	2,620 Avg.
Latex Interior Flat													
Shipments – Gallons	18,960	26,910	27,710	61,900	53,695	96,800	74,945	51,260	48,410	20,690	18,690	24,430	524,400
Production – Gallons	43,700	43,700	43,700	43,700	43,700	43,700	43,700	43,700	43,700	43,700	43,700	43,700	524,400
Inv. gal (Cumulative)	92,030	108,820	124,810	106,610	96,615	43,515	12,270	4,710	–	23,010	48,020	67,290	60,642 Avg.
Total Inv. (incl. 26,220 gal S.S.)	118,250	135,040	151,030	132,830	122,835	69,735	38,490	30,930	26,220	49,230	74,240	93,510	86,862 Avg.
Alkyd Semi-Gloss													
Shipments – Gallons	8,095	11,485	11,825	26,490	22,940	41,320	31,990	21,875	20,660	8,825	7,975	10,420	223,900
Production – Gallons	18,660	18,660	18,655	18,660	18,660	18,655	18,660	18,660	18,655	18,660	18,660	18,655	223,900
Inv. Bal. (Cumulative)	39,320	46,495	53,325	45,495	41,215	18,550	5,220	2,005	–	9,835	20,520	28,755	25,895 Avg.
Total Inv. (incl. 11,195 gal S.S.)	50,515	57,690	64,520	56,690	52,410	29,745	16,415	13,200	11,195	21,030	31,715	39,950	37,090 Avg.

TABLE 90 (continued)

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Total
Alkyd Gloss Enamel													
Shipments – Gallons	3,685	5,235	5,390	12,100	10,475	18,880	14,610	9,990	9,435	4,020	3,630	4,750	102,200
Production – Gallons	8,515	8,515	8,520	8,515	8,515	8,520	8,515	8,515	8,520	8,515	8,515	8,520	102,200
Inv. Bal. (Cumulative)	17,980	21,260	24,390	20,805	18,845	8,485	2,390	915	–	4,495	9,380	13,150	11,841 Avg.
Total Inv. (incl. 5,110 gal S.S.)	23,090	26,370	29,500	25,915	23,955	13,595	7,500	6,025	5,110	9,605	14,490	18,260	16,951 Avg.
Total – Trade Sales													
Shipments – Gallons	41,215	58,470	60,220	134,740	116,770	210,415	162,905	111,410	105,215	44,950	40,610	53,080	1140,000
Production – Gallons	95,000	95,000	95,000	95,000	95,000	95,000	95,000	95,000	95,000	95,000	95,000	95,000	1140,000
Inv. Bal. (Cumulative)	200,145	236,675	271,455	231,715	209,945	94,530	26,625	10,215	–	50,050	104,440	146,360	131,846 Avg.
Total Inv. (incl. 57,000 gal S.S.)	257,145	293,675	328,455	288,715	266,945	151,530	83,625	67,215	57,000	107,050	161,440	203,360	188,846 Avg.
Industrial													
Shipments – Gallons	63,330	63,330	63,340	63,330	63,330	63,340	63,330	63,330	63,340	63,330	63,330	63,340	760,000
Production – Gallons	63,330	63,330	63,340	63,330	63,330	63,340	63,330	63,330	63,340	63,330	63,330	63,340	760,000
Inv. Bal. (Cumulative)	–	–	–	–	–	–	–	–	–	–	–	–	–
Total Inv. (incl. 38,000 gal S.S.)	38,000	38,000	38,000	38,000	38,000	38,000	38,000	38,000	38,000	38,000	38,000	38,000	38,000 Avg.
Total Plant													
Shipments – Gallons	104,545	121,800	123,560	198,070	180,100	273,755	226,235	174,740	168,555	108,280	103,940	116,420	1900,000
Production – Gallons	158,330	158,330	158,340	158,330	158,330	158,340	158,330	158,330	158,340	158,330	158,330	158,340	1900,000
Inv. Bal. (Cumulative)	200,145	236,675	271,455	231,715	209,945	94,530	26,625	10,215	–	50,050	104,440	146,360	131,846 Avg.
Total Inv. (incl. 95,000 gal S.S.)	295,145	331,675	366,455	326,715	304,945	180,530	121,625	105,215	95,000	145,050	199,440	241,360	226,846 Avg.

TABLE 91

MODEL PLANT
BALANCE SHEET
(Year Ending December 31, 19–2)

ASSETS

Current Assets			
Cash		($ 14,512)	
Accounts Receivable (Dec. Sales)		391,929	
Inventories:			
Finished Goods			
Trade-203,360 gal @ $2.73/gal	$ 555,173		
Industrial-38,000 gal @ 2.52/gal	95,760		
Raw Materials ($^{1}/_{12}$ Of Annual Cost)	229,439		
Packages, Etc. ($^{1}/_{12}$ Of Annual Cost)	52,659		
Total Inventories		$ 933,031	
Total Current Assets			$ 1,310,448
Property, Plant & Equipment			
Land	$ 100,000		
Buildings	2,353,450		
Equipment	1,277,150		
Total (On The Basis Of Cost)		$ 3,730,600	
Less Allowance For Depreciation		314,268	
Total Property, Plant & Equipment			$ 3,416,332
TOTAL ASSETS			$ 4,726,780

LIABILITIES & SHAREHOLDERS' EQUITY

Current Liabilities		
Accounts Payable ($^{1}/_{12}$ Of R.M. & Pkg. Cost)	$ 282,098	
Income Taxes (¼ Of 342,531)	85,633	
Total Current Liabilities		$ 367,731
Long Term Debt		
Bank Loan ($4,000,000 - - 10 yr Term - 7%)		3,200,000
Shareholders' Equity		
Common Stock		
100,000 Shares @ $10	$ 1,000,000	
Retained Earnings	159,049	
Total Shareholders' Equity		$ 1,159,049
TOTAL LIABILITIES & SHAREHOLDERS' EQUITY		$ 4,726,780

TABLE 92

MODEL PLANT
CASH FLOW STATEMENT
(1.9 Million Gallons Sold & Manufactured)
(Year 19–2)

REVENUE: NET		$6,604,400
EXPENDITURES (CASH)		
Raw Materials, Packages, Etc.	$3,385,179	
Salaries & Wages	680,061	
Other Mfg. Expenses	798,000	
S, G & A	761,141	
Interest Expense	252,000	
Federal Income Tax	285,443	
State & Local Taxes	57,088	
Principal Payment Long-Term Debt	400,000	
		6,618,912
NET CASH FLOW		$ (14,512)

TABLE 93

MODEL PLANT
RETURN ON INVESTMENT
(Year 19–2)

Return on investment is calculated using four of the more common methods. The first three methods are essentially asset efficiency measurements while the last method centers attention on the rate of return that will be earned by the business owners.

1. Total Gross Assets Available Method

$$\frac{\text{Income Before Interest}}{\text{Total Gross Assets}} = \frac{\$329{,}154}{\$5{,}041{,}048} = 6.53\%$$

2. Total Net Assets Available Method

$$\frac{\text{Income Before Interest}}{\text{Total Net Assets}} = \frac{\$329{,}154}{\$4{,}726{,}780} = 6.96\%$$

3. Stockholders' Equity Plus Long-Term Debt Method

$$\frac{\text{Income Before Interest}}{\text{Stockholders' Equity Plus Long Term Debt}} = \frac{\$329{,}154}{\$4{,}359{,}049} = 7.55\%$$

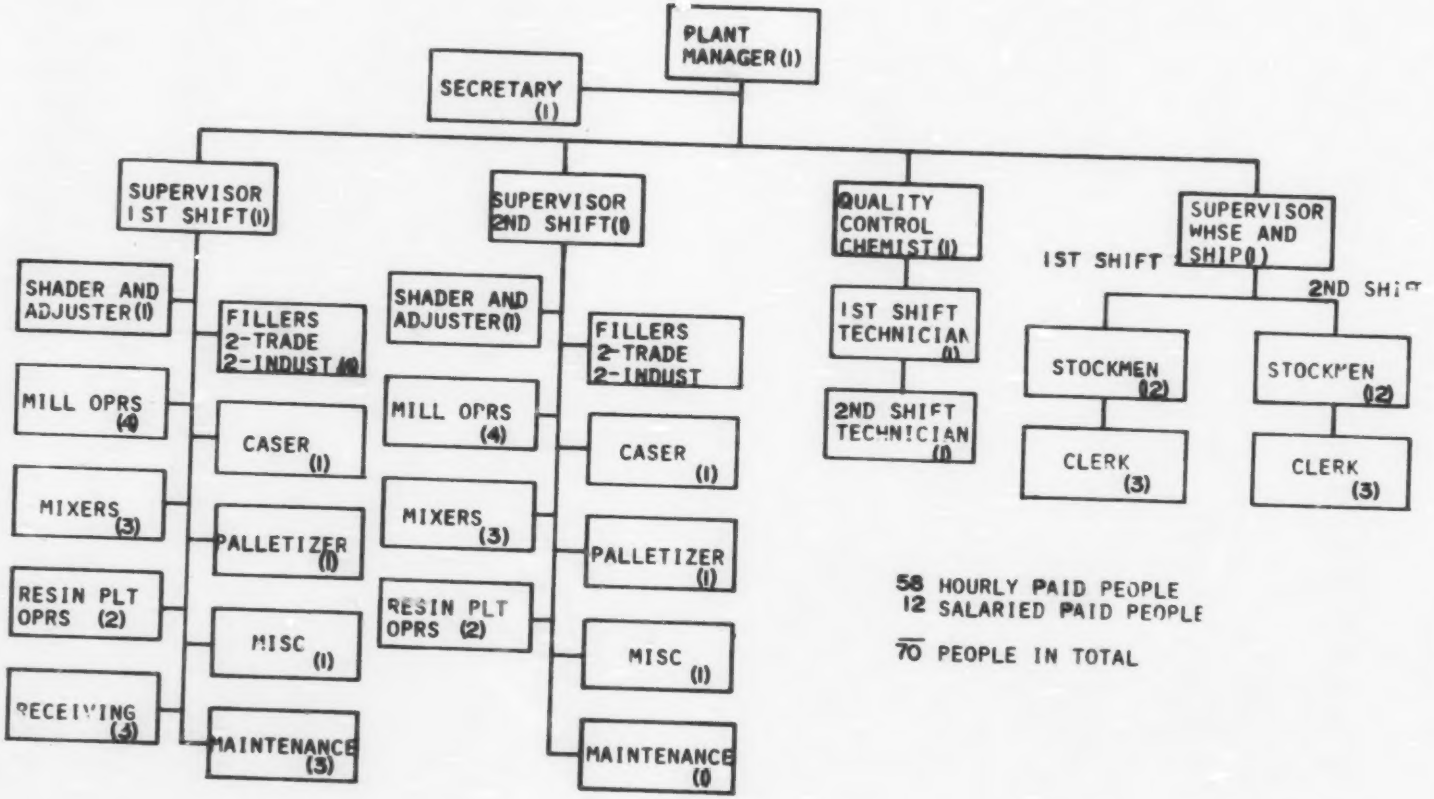
4. Stockholders' Equity Method

$$\frac{\text{Net Income}}{\text{Stockholders' Equity}} = \frac{\$228{,}354}{\$1{,}159{,}049} = 19.70\%$$

TABLE 94

MODEL PLANT
1.9 MILLION GALLON FINISHED OUTPUT

	Latex			Alkyd				
	House Paint	Flat Wall	Total	Exterior Trim	Interior Semi-Gloss	Interior Gloss	Total	Grand Total All
Whites & Tint Bases	232,000	440,000	672,000	6,500	204,400	72,100	283,000	955,000
Tints Produced from Bases								
Light Ivory	–	31,000	31,000	–	9,500	800	10,300	41,300
Ivory	800	1,300	2,100	–	800	800	1,600	3,700
Cream	–	1,500	1,500	–	1,100	1,000	2,100	3,600
Yellow	1,100	1,100	2,200	–	1,500	2,100	3,600	5,800
Light Green	1,900	800	2,700	–	600	1,500	2,100	4,800
Medium Green	2,300	1,000	3,300	–	800	–	800	4,100
Light Blue	–	1,100	1,100	–	400	1,000	1,400	2,500
Medium Blue	–	400	400	800	400	4,200	5,400	5,800
Pink	–	800	800	–	400	–	400	1,200
Light Gray	1,300	1,100	2,400	–	600	2,700	3,300	5,700
Medium Gray	1,300	–	1,300	–	–	–	–	1,300
Off-White	800	44,300	45,100	–	3,400	–	3,400	48,500
Total Tints	9,500	84,400	93,900	800	19,500	14,100	34,400	128,300
Total Whites, Bases & Tints	241,500	524,400	765,900	7,300	223,900	86,200	317,400	1,083,300
Solid Colors								
Olive	7,200	–	7,200	1,300	–	–	1,300	8,500
Green	2,700	–	2,700	2,100	–	3,400	5,500	8,200
Red	5,500	–	5,500	1,100	–	6,100	7,200	12,700
Brown	8,000	–	8,000	2,300	–	2,500	4,800	12,800
Charcoal	5,300	–	5,300	1,000	–	1,300	2,300	7,600
Black	3,400	–	3,400	–	–	2,700	2,700	6,100
Blue	–	–	–	800	–	–	800	800
Total Solid Colors	32,100	–	32,100	8,600	–	16,000	24,600	56,700
Total All Trade Sales	273,600	524,400	798,000	15,900	223,900	102,200	342,000	1,140,000
Industrials (no breakdown by product line) (50% of industrials alkyd based)								760,000
Total Plant Finished Output								1,900,000
Internal Production of Alkyd Resins (2,166,000 lb @ 50% NVM)								



58 HOURLY PAID PEOPLE
12 SALARIED PAID PEOPLE

70 PEOPLE IN TOTAL

FIGURE 73

MODEL PLANT
FACTORY MANNING CHART
(FINISHED OUTPUT 1.9 MILLION GALLONS)

TABLE 95

MODEL PAINT PLANT COST, DOLLARS

Item	Total Material	Total
Summary		
Equipment		
Paint Plant	521,900	
Resin Plant	222,500	
Storage	211,600	
Miscellaneous	142,750	
Sub-Total	1,098,750	1,098,750
Utilities	178,400	178,400
Sub-Total	1,277,150	1,277,150
Building		
Sitework	167,100	
Part I - Raw Material Warehouse	219,700	
Part II - Manufacturing Building	919,450	
Part III - Finished Goods Warehouse	526,700	
Sub-Total	1,825,950	1,825,950
Total		3,103,100
Freight and Sales Tax		124,400
Engineering - 7%		217,200
Contingency - 10%		310,300
Project Total*		3,755,000

* Based on Chicago ENR Construction Cost Index of 1964 for December, 1972.

TABLE 96

MODEL PAINT PLANT COST, DOLLARS

Item	Total Material	Total
Equipment and Utilities Summary		
Equipment		
Paint Plant		
Pebble Mills	128,150	
Ball Mills	37,500	
Sand Mills	26,500	
High Speed Dispersers	44,800	
Mixing and Finishing Tanks	166,450	
Filling and Packaging	105,000	
Laboratory	13,500	
Sub-Total	521,900	521,900
Resin Plant	222,500	
Storage	211,600	
Miscellaneous	142,750	
Sub-Total	576,850	576,850
Utilities	178,400	178,400
Total		1,277,150

TABLE 97

MODEL CONTROLLED PLANT
DEPRECIATION SCHEDULE
(Finished Output 1.9 Million Gallons)

	Asset Capitalized Value	Straight Line Depr. %	Annual Depr. Amount
LAND	$ 100,000	—	—
BUILDING & SITE PREPARATION:			
Raw Material Warehouse	219,700	1.25	$ 2,746
Manufacturing Building	912,450	1.25	11,406
Finished Goods Warehouse	526,700	1.25	6,584
Site Preparation	167,100	1.25	2,089
Engineering	217,200	1.25	2,715
Other Building Costs	310,300	1.25	2,879
Total Buildings, Etc.	$2,353,450		$ 29,419
EQUIPMENT & UTILITIES:			
Paint Plant	$ 521,900	10.00	$ 52,190
Resin Plant	222,500	10.00	22,250
Storage	211,600	10.00	21,160
Miscellaneous	142,750	10.00	14,275
Utilities	178,400	10.00	17,840
Resin Plant Afterburner	26,000	10.00	2,600
Paint Plant Baghouse	7,350	10.00	735
Total Equipment & Utilities	$1,310,500		$ 160,469
GRAND TOTAL	$3,763,950		$ 160,469

Note:

1. All freight & sales tax was assumed to be expensed in prior year.
2. Assumption is that plant is operating and on stream: All start-up costs have expired in prior years.
3. Depreciation will be allocated between trade and industrial products on 60% to 40% basis.

Trade	60%	$ 96,281
Industrial	40%	64,188
		$160,469

TABLE 98

MODEL CONTROLLED PLANT
INCOME STATEMENT
(Year Ending December 31, 19–2)

	Trade Sales Products	Industrial Sales Products	Total All
REVENUE (NET)			
A) 1,140,000 gal @ $3.78/gal	$4,309,200	—	$4,309,200
A) 760,000 gal @ $3.02/gal	—	$2,295,200	2,295,200
Total Revenue	$4,309,200	$2,295,200	$6,604,400
COST OF GOODS SOLD			
Raw Materials (See Table 85)	$1,550,228	$1,203,045	$2,753,273
Packaging (See Table 86)	447,078	184,828	631,906
Salaries & Wages (See Table 87)	447,051	233,010	680,061
Depreciation (See Table 88)	96,281	64,188	160,469
B) Other Manufacturing Costs			
Trade-Estimated @ 50¢/gal	570,000	—	570,000
Industrial-Estimated @ 30¢/gal	—	228,000	228,000
C) Operating Cost-Resin Reactor Afterburner	4,476	1,119	5,595
C) Baghouse Operating Cost	192	106	298
	$3,115,306	$1,914,296	$5,029,602
Gross Profit	$1,193,894	$ 380,904	$1,574,798
SELLING, GENERAL & ADMINISTRATIVE EXPENSES			
Trade-Estimated @ 15% of Sales	$ 646,380	—	$ 646,380
Industrial-Estimated @ 5% of Sales	—	$ 114,761	114,761
Total S, G & A Expense	$ 646,380	$ 114,761	$ 761,141
Operating Income	$ 547,514	$ 266,143	$ 813,657
INTEREST EXPENSE			
Long-Term Debt	$ 152,461	$ 101,641	$ 254,101
Income Before Taxes	$ 395,053	$ 164,503	$ 559,556
INCOME TAXES			
Federal Income Tax (50%)	$ 197,527	$ 82,251	$ 279,778
State & Local Taxes (10%)	39,505	16,450	55,955
Total Taxes	$ 237,032	$ 98,701	$ 335,733
NET INCOME	$ 158,021	$ 65,802	$ 223,823

TABLE 98
(Continued)

MODEL CONTROLLED PLANT
INCOME STATEMENT
(Year Ending December 31, 19–2)

Notes:

A) Selling price calculated as follows using data from current industrial reports, M28F - - year 1971.

TRADE -$1,563 million divided by 431 million gal = $3.63/gal
$3.63/gal times growth rate of 4% = $3.78/gal

INDUSTRIAL -$1,268 million divided by 443 million gal = $2.86/gal
$2.68/gal times growth rate of 5.5% = $3.02/gal

B) The estimated other manufacturing costs is to cover such items as:

1. Repair parts which are expensed
2. Operating, heating and utility costs
3. Property insurance and taxes
4. Miscellaneous operating expenses

C) See Table 102.

TABLE 99

MODEL CONTROLLED PLANT
BALANCE SHEET
(Year Ending December 31, 19–2)

ASSETS

Current Assets			
Cash		($ 19,043)	
Accounts Receivable (Dec. Sales)		391,929	
Inventories:			
Finished Goods			
Trade-203,360 gal @ $2.73/gal	$ 555,173		
Industrial-38,000 gal @ 2.52/gal	95,760		
Raw Materials (1/12 Of Annual Cost)	229,439		
Packages, Etc. (1/12 Of Annual Cost)	52,659		
Total Inventories		$ 933,031	
Total Current Assets			$ 1,305,917
Property, Plant & Equipment			
Land	$ 100,000		
Buildings	2,353,450		
Equipment	1,277,150		
Air Emission Control Devices	33,350		
Total (On The Basis Of Cost)		$ 3,763,950	
Less Allowance For Depreciation		320,938	
Total Property, Plant & Equipment			$ 3,443,012
TOTAL ASSETS			$ 4,748,929

LIABILITIES & SHAREHOLDERS' EQUITY

Current Liabilities		
Accounts Payable (1/12 Of R.M. & Pkg. Cost)	$ 282,098	
Income Taxes (¼ Of 335,733)	83,933	
Total Current Liabilities		$ 366,031
Long-Term Debt		
Bank Loan ($4,033,350 - - 10 yr Term - 7%)		3,226,680
Shareholders' Equity		
Common Stock		
100,000 Shares @ $10	$ 1,000,000	
Retained Earnings	156,218	
Total Shareholders' Equity		1,156,218
TOTAL LIABILITIES & SHAREHOLDERS' EQUITY		$ 4,748,929

TABLE 100

MODEL CONTROLLED PLANT
CASH FLOW STATEMENT
(1.9 Million Gallons Sold & Manufactured)
(Year 19–2)

REVENUE: NET		$6,604,400
EXPENDITURES (CASH)		
Raw Materials, Packages, Etc.	$3,385,179	
Salaries & Wages	680,061	
Other Mfg. Expenses	798,000	
S, G & A	761,141	
Interest Expense	254,101	
Federal Income Tax	279,778	
State & Local Taxes	55,955	
Principal Payment Long-Term Debt	403,335	
Operating Cost of Emission Controls	5,893	
		6,623,443
NET CASH FLOW		$ (19,043)

TABLE 101

MODEL CONTROLLED PLANT
RETURN ON INVESTMENT
(Year 19–2)

Return on investment is calculated using four of the more common methods. The first three methods are essentially asset efficiency measurements while the last method centers attention on the rate of return that will be earned by the business owners.

1) Total Gross Assets Available Method

$$\frac{\text{Income Before Interest}}{\text{Total Gross Assets}} = \frac{\$325{,}463}{\$5{,}069{,}867} = 6.42\%$$

2) Total Net Assets Available Method

$$\frac{\text{Income Before Interest}}{\text{Total Net Assets}} = \frac{\$325{,}463}{\$4{,}748{,}929} = 6.85\%$$

3) Stockholders' Equity Plus Long-Term Debt Method

$$\frac{\text{Income Before Interest}}{\text{Stockholders' Equity Plus Long-Term Debt}} = \frac{\$325{,}463}{\$4{,}382{,}898} = 7.43\%$$

4) Stockholders' Equity Method

$$\frac{\text{Net Income}}{\text{Stockholders' Equity}} = \frac{\$223{,}823}{\$1{,}156{,}218} = 19.36\%$$

TABLE 102

MODEL CONTROLLED PLANT
AIR EMISSION CONTROL DEVICES

RESIN REACTOR AFTERBURNER:

	1200 SCFM Thermal Type	1200 SCFM Catalytic Type	Average of Two
A) Capital Cost - (Includes Installation)	$25,000	$27,000	$26,000
B) Operating Cost Per Year - 16 hrs/day	6,850	4,340	5,595
Effect On Yield	None	None	None

Note (A)

Capital cost is assumed to be financed with long-term debt and as part of initial financing arrangements.

Note (B)

Operating cost is apportioned between trade sales and industrial finishes. Products on same ratio as manufactured resins are used within the finished products. This will be 80% trade and 20% industrial.

PAINT PLANT BAGHOUSE:

	Pulse Test Type	Shaker Type	Average of Two
C) Capital Cost - (Includes Installation)	$ 6,800	$ 7,900	$ 7,350
D) Operating Cost Per Year - 8 hr/day (Includes Maintenance, Utilities, Etc.)	350	245	298
D) Pigment Recovered Per Year	2,850 lb	2,850 lb	2,850 lb

Note (C)

Same assumption on capital cost as indicated in Note A above.

Note (D)

Operating cost and credit for pigment recovered will be apportioned between trade sales and industrial finishes on the same ratio as pigment used between the two. This will be 64.5% for trade and 35.5% for industrials.

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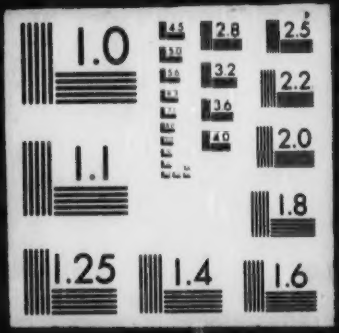

CHAPTER 8

PIGMENT INDUSTRY

I. INTRODUCTION

Pigments represent one of the major building blocks in the formulation of an acceptable coating. Historically, the use of coloring agents was largely for decorative effect. While this is still of major importance today, pigments are now recognized to produce a variety of other important properties in paint films. The selection of the correct pigment for a given application must take into account factors other than coloring ability alone. Pigments can be used which improve the physical properties of both the liquid paint and the final paint film. They can act as corrosion inhibitors and as mildew inhibitors. Some pigments have the ability to absorb ultraviolet radiation and so protect the paint film as well as the coated material from degradation from this source. Pigments may react chemically with the binder to produce desirable (and sometimes undesirable) effects. Finally, and this has become more important in recent years, the biological effect of the pigment material must be taken into account.

The feature which distinguishes a pigment from other coloring agents is its insolubility in the medium in which it is employed. A pigment may be defined as a solid material, present in the form of small particles, which is essentially insoluble in the medium in which it is present. The ability to color or opacify the medium is not considered essential to the definition. As will be seen later, a class of pigments called extenders is used which impart little or no color or opacity even when used in large amounts.

A coloring agent which is soluble in its medium is called a dye. Some of the organic pigments such as wood stains could more properly be classed as dyes. Two other types of coloring agents are "lakes" and "toners". A lake is a water insoluble pigment formed from coloring matter in the presence of a substrate. If the formation takes place without a substrate, the coloring agent is called a toner. Lakes and toners are usually organic.

A. Classification and Statistics[3]

Pigments represent one of the most important raw materials consumed by the paint and

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coating industry. On a weight basis, consumption of pigments exceeded that of any other single class of raw materials. In 1970, the coatings industry used 1,727 thousand tons of pigments of all types. Consumption of solvents was a close second at 1,695 thousand tons.

In addition to their use in paints, pigments find extensive use in other industries such as rubber, paper, plastics and printing. In fact, consumption by the paint industry represents only about half the total pigment production in this country. Total pigment production in 1968 stood at 3,640.6 thousand tons. Production by major categories for 1968 is presented in Table 103. In addition to those listed, an estimated 52,500 tons of metallic pigments, mostly zinc and aluminum, were consumed by the paint industry in 1970.

The black organic pigments consist almost entirely of carbon blacks produced from petroleum feed stocks. Inorganic blacks are primarily black iron oxide.

The white pigments fall into two classes:[2] hiding (opaque) and extender (non-opaque) pigments. The extenders are not pigments in the usual sense of the word. That is, they do not add color or opacity to the paint film. Their lack of these properties is due to their relatively low index of refraction. Historically, the extenders were introduced as a cheap substitute for the more expensive true pigment. Extenders, today, are recognized to contribute to stability, texture, durability and a variety of other paint properties. Production of the important white hiding and extender pigments is given in Table 104.

The organic color pigments, almost entirely synthetic, include a wide variety of types.[2, 3] The one feature most of the organic dyes and pigments have in common is the presence of ring structures in their molecules. The most common starting materials are benzene, toluene, xylenes, naphthalene and anthracene. Reactions such as nitration, halogenation, and sulfonation are used to transform these materials into the intermediates from which the final dye or pigment is produced. Generally speaking, a dye is a coloring material which is soluble in the medium in which it is employed while a pigment consists of discrete particles which are insoluble in the medium. It is not uncommon for an organic coloring agent to be soluble in one medium and insoluble in another. Thus, it may act as either a dye or a pigment.

No single organic pigment, or class of pigments, accounts for more than a relatively small fraction of the total. Production of the major types is shown in Table 105.

Within any given type, there exists a large variety of pigments. For instance, among the azo group there are at least 22 different pigment materials having little in common except the presence of a (— N = N —) bridge between aromatic groups. Most colors, except white, are

TABLE 103

PIGMENT PRODUCTION BY MAJOR TYPE[3]

Pigment	1968 Production (1,000 ton/yr)
Black Organic	66.5
Black Inorganic	3.6
White Hiding	682.3
White Extender	2,670.1
Colored Organic	27.1
Colored Inorganic	191.0
Total	3,640.6

TABLE 104

MAJOR WHITE PIGMENTS[3]

Pigment	1968 Production (1,000 ton/yr)
Hiding	
Titanium Dioxide	623.7
Zinc Oxide (lead free)	36.4
White Lead	11.1
Leaded Zinc Oxide	11.1
Extender	
Kaolin (China clay)	2,153.0
$CaCO_3$, precipitated	226.0
Talc	205.2
Bartyes	60.9
Mica	25.0

TABLE 105

PRODUCTION OF ORGANIC PIGMENTS[3]

Organic Pigment	1968 Production (1,000 ton)
Insoluble Azo	7.0
Soluble Azo	6.8
Phthalocyanine	6.0
Condensation Acid	2.5
Basic	1.7
Miscellaneous	2.6

TABLE 106

PRODUCTION OF MAJOR INORGANIC COLOR PIGMENTS[3]

Pigment	1968 Production (1,000 ton/yr)
Synthetic Iron Oxide	72.4
Natural Iron Oxide	57.6
Chromate	44.2
Ferrocyanide	6.0
Sulfide	3.0
Mixed Chromate and Ferrocyanide	2.8

available with the organics. Their principal disadvantages are high cost and inferior light, heat and chemical stability.

The inorganic color pigments include several important types. Production of the major types is given in Table 106. As a group, the inorganics are less expensive and possess higher stability than the organics. They are considered more suitable for exteriors and for environments where high temperatures or corrosive conditions are encountered. They do not possess the range of colors and tones of the organic pigments, but have representatives in most of the major color groups.

B. Purpose and Scope

The purpose of this study is to identify, and study further, those pigment groups which represent major contributors to air pollution. This decision is based on several factors. First, it is impossible from a time standpoint to study in detail all of the pigments used by the coating industry. It becomes necessary, then, to concentrate effort on those areas where the problem is most acute. This is reasonable on technical grounds, also; since many of the production processes used are by their nature relatively free of air emissions. Also, some pigments are produced in such small amounts that diversion of effort to these would be unjustified.

An initial screening was done to eliminate certain groups from consideration. The production of the carbon black pigments is included in a separate EPA study and so will not be studied here. The production of white lead and leaded zinc oxide will not be considered, in spite of lead's potential toxicity, since present and future regulations on lead content in paint should virtually eliminate these pigments for the coatings industry. Recent trends, as well as industry projections, support this conclusion. Paint industry projections predict the use of white lead to decrease to 20% of its 1970 value by 1975.[31]

The white extenders have been eliminated on several grounds. They are produced primarily by mining operations followed by grinding, classification, drying, etc. Any problems which might exist would be of a particulate nature. Technology for particulate control is well developed and the extender industry does not present any unique problems. Furthermore, the extenders are considered non-toxic with one possible exception.

Certain types of talc contain asbestos fibers known as "tremolyte". Asbestos fibers including tremolyte are subject to very strict airborne concentration limitations. Not all varieties of talc contain tremolyte and those that do contain varying amounts. New York State talc may contain 10% to 30% tremolyte, Montana talc less than 1%, and Georgia steatite talc (soapstone) 10%. The extent of the toxicity problem associated with tremolyte has not yet been agreed upon. In any event, it is not known to what extent tremolyte is present in the talc used by the paint industry.

The organic pigments have been eliminated from consideration also. No single organic pigment is produced in sufficient quantity to be a significant factor in the total emissions picture. Furthermore, the processes used are largely liquid phase reactions under fairly mild conditions. Air pollution problems on either a total emission basis or on a per unit product basis should be quite low. Many of the compounds involved in manufacture are considered hazardous to humans, however, so that there may exist occupational safety problems but such problems are not within the scope of this study.

The pigments being studied in some detail include, among the whites, titanium dioxide and zinc oxide. Among the inorganic color pigments the iron oxides, the chrome pigments and the cadmiums are included. The cadmiums are present by virtue of their potential toxicity rather than production volume. The following sections will detail the work that has been completed on these pigments to date.

II. REVIEW OF MAJOR PIGMENTS

A. Cadmium Pigments[32,33]

A visit was made to the offices of Harshaw Chemical Company on June 29, 1972 to discuss the manufacturing of cadmium pigments. Harshaw is one of the two major producers of cadmium pigments and has two plants which are located in Elyria, Ohio and Louisville, Kentucky. They produce 20 cadmium lithopone yellows, 20 cadmium lithopone reds, 32 full strength cadmium yellows and 64 full strength cadmium reds. They also market but do not produce 12 mercury cadmium lithopone reds and 12 full strength mercury cadmium reds. The colors produced range from primrose yellow to dark maroon. The pure cadmium sulfide is a deep orange color. The color variations are achieved by the addition of controlled amounts of zinc sulfate for the yellows and selenium compounds for the reds as shown below:

Zinc Sulfide Addition ⟵ CdS ⟶ Selenium Addition

Primrose ← Lemon ← Golden ⟵ Orange ⟶ Lt Reds → Dark Reds → Maroon

The cadmium lithopone pigments contain barium sulfate as a diluent and offer better tinting strength and hiding power on a equal cost basis with the high strength pigments. They are used primarily where higher pigment loadings can be tolerated.

The full strength pigments have approximately twice the tinctorial strength of the lithopone types and are used primarily in the manufacturing of plastic color concentrate where low pigment concentration and maximum hiding in thin films are desired.

The mercury cadmium pigments are similar in color to the cadmium sulfoselenide oranges and reds but are mixtures of mercury sulfide with cadmium sulfide. They are slightly lower in cost but resistance to heat, moisture and exterior weathering is not quite as good as the cadmium sulfoselenides.

Use of cadmium pigments in trade sale products is limited almost exclusively to artist paints. Because of its high cost, it is used primarily for high quality industrial finishes where its heat resistance and good weather ability are required. Typical applications would be for high temperature bake enamel finishes and commercial airline and automotive finishes.

A simplified block flow diagram for the production of cadmium sulfide as it pertains to potential emissions is given as Figure 74.

The cadmium pigments are prepared by reacting an aqueous solution of cadmium sulfate, $CdSO_4$, (or cadmium chloride) with a solution of sodium sulfide, Na_2S, (or H_2S) in a stirred reactor. Zinc sulfate or selenium may be added in the reactor or calciner to obtain the various shades. The precipitate is filtered, washed, calcined, wet ground in a ball mill, dried in a shelf type steam heated oven and dry ground in a hammer mill. Cadmium lithopones are produced in the same manner except the starting materials are cadmium sulfate and barium sulfide and the precipitate is a cadmium sulfide — barium sulfate mixture.

The cadmium sulfate solution is produced by dissolving cadmium bar stock or sponge in sulfuric acid containing some nitric acid in a percolating tower at about 30°C. Flower of sulfur is sometimes added to the calciner and results in an SO_2 emission at the gas exit end.

This manufacturing process produces the following emissions:[32,33]

Percolating Tower	CdO — About 0.2% of charge
	NO_2 — Amount unknown
	SO_3 — Amount unknown
Calciner	CdS — About 1.2% of cadmium charge
	Selenium — Amount unknown
	ZnS — Amount unknown
	SO_2 — Amount unknown
Calciner Scrubber	Liquid water-to-sewage pretreatment. Uncollected emission — amount unknown but considered insignificant

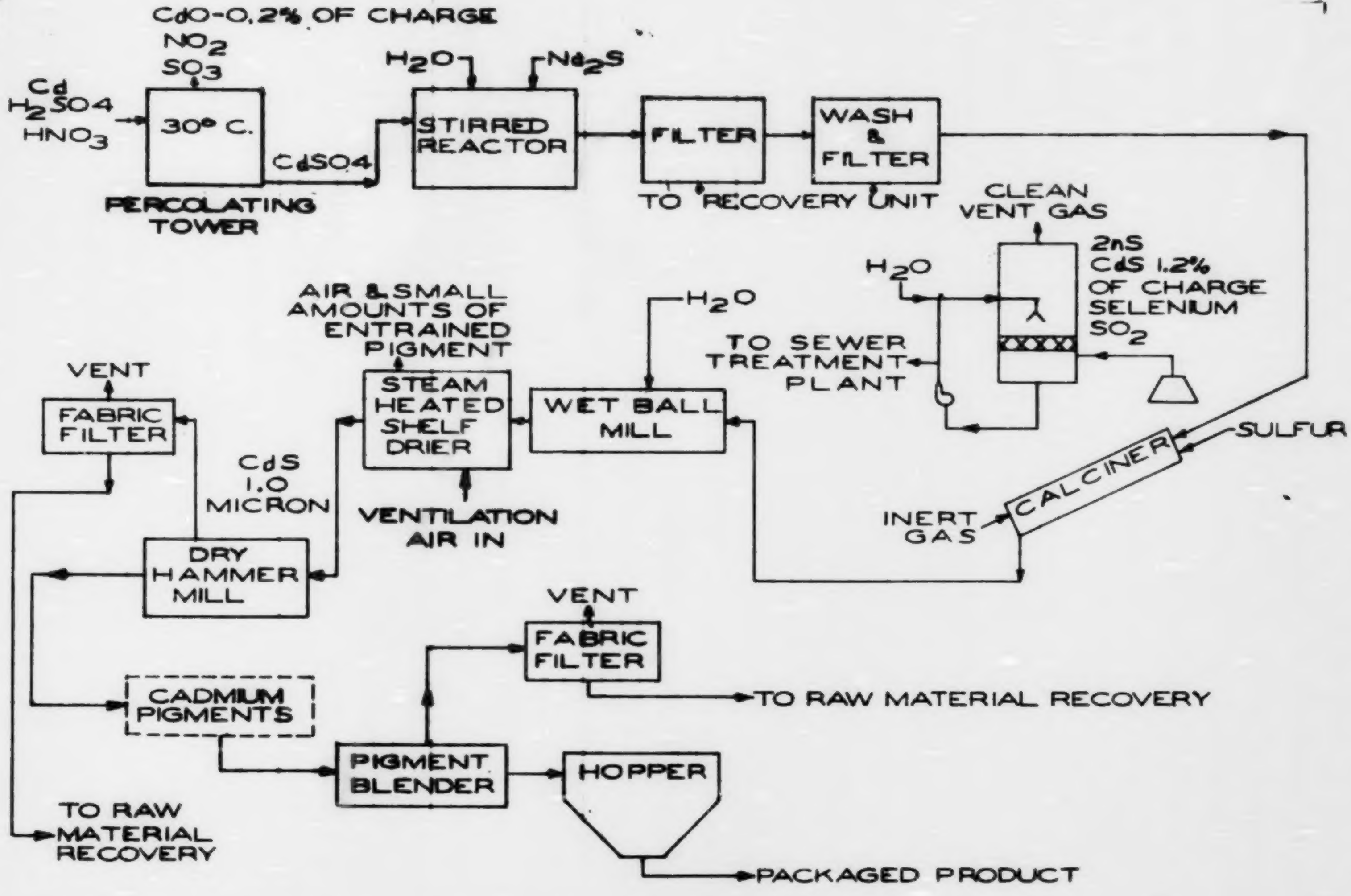

Figure 74· Flow diagram for cadmium sulfide production

Oven Drier	Some entrained pigment but not a significant emission
Dry Hammer Mill and Product Blender	Particulate pigment emission but collected in a fabric filter for recycle raw material. Cannot be used for product due to color contamination. Raw material costs high enough to make recovery economically desirable.

In as much as the contribution of environmental pollution from manufacturing of cadmium pigment is miniscule compared to a great number of other pigments, the only justification for studying it in place of these other pigments would be its potential as a health hazardous chemical. This problem was discussed with Harshaw. They are quite concerned, as one might expect, that cadmium could be, in their opinion, erroneously labeled a health hazardous material. They went to considerable length to point out that practically no cadmium pigments are used in trade sales coatings, that cadmium pigments are manufactured as insoluble cadmium sulfide (0.000001 gram/ 100 ml) and are non-toxic due to their insolubility and that emissions in the manufacturing process are cadmium oxide and sulfide. Cadmium oxide is also considered an insoluble compound but no data was given.

Harshaw is very interested in cooperating with the EPA in any way. They would be glad to let the EPA source test their plants and are quite interested to learn about any information the EPA may have on toxicity of cadmium, especially chronic poisoning. They can furnish a bibliography on all work published to date on cadmium toxicity. They also mentioned that the NPCA is sponsoring a study for the Fall of 1972 on the toxicity of 23 heavy metals at the Kettering Institute.

B. Zinc Oxide[2,3,34,35]

Zinc oxide, either leaded or unleaded, is one of the most important white color pigments used by the coating industry. While its optical properties are inferior to those of titanium dioxide, it is able to maintain its position in the paint industry through its ability to impart a variety of desirable properties to paint films. Also, it is an effective fungistat and mildewcide.

Use of zinc oxide by the paint industry had been declining somewhat in recent years since it was not compatible with the latex type paints then being formulated. Its situation is beginning to improve again and paint industry projections predict an increase in zinc oxide use of about 4% per year over the next several years.[31] Zinc oxide production in 1969 was about 220,000 tons. The U.S. paint industry accounts for an estimated 35,000 tons of this production. Other major uses include the rubber, pottery and glass industries.

Zinc oxide itself is considered non-toxic. Leaded oxides have a toxicity in proportion to the amount of lead present. The use of leaded zinc oxide is decreasing rapidly and is expected to continue to do so.

There are three principle methods used in the manufacture of zinc oxide: the French, modified American and the Electrothermal.

In the French process, metallic zinc is vaporized in a retort under a reducing atmosphere. The zinc vapor is then burned in a combustion chamber to give zinc oxide particles which are blown through cooling pipes and then collected in baghouses and packaged. In this process, the furnace gases do not come into contact with the zinc oxide production system. A flow sheet is presented in Figure 75.

The American process starts with zinc ore. The two types used are franklinite (ZnO) and sphalerite (ZnS). Franklinite has the advantages of being almost free from lead impurities as well as not requiring a roasting operation to remove sulfur. Sphalerite is more available, however, and most of the oxide produced by the American process uses this as its starting material. Some franklinite is still used, however. In addition to lead, other common impurities include iron, cadmium and manganese. Cadmium and lead are usually produced as by-products in zinc processing operations.

A typical flow sheet for the American process is shown in Figure 76. A ZnS ore concentrate is roasted in air to remove the sulfur and a portion of the lead and cadmium. The solid product from the roaster is mixed with some fluxes and coke and fed to a sintering machine where it is sintered at temperatures as high as 1600°C but usually 1100 to 1200°C. Most of the remaining lead and cadmium are released in the form of oxide particles which are collected with electrostatic precipitation or in a fabric filter.

The product from the sintering machine is crushed, mixed with coke and fed to a furnace where the zinc oxide is reduced and the vaporized zinc subsequently re-oxidized. The ZnO is collected, calcined again to remove residual impurities and/or control particle size and packaged.

The electrothermal process is similar to the American process except for the furnace. In this case, the product from the sintering machine is mixed with coke and charged to an electrical resistance furnace. Electrodes are inserted into the charge which serves as the resistance. The zinc vapor and CO leaving the furnace are oxidized by air entering at the furnace exit. The product

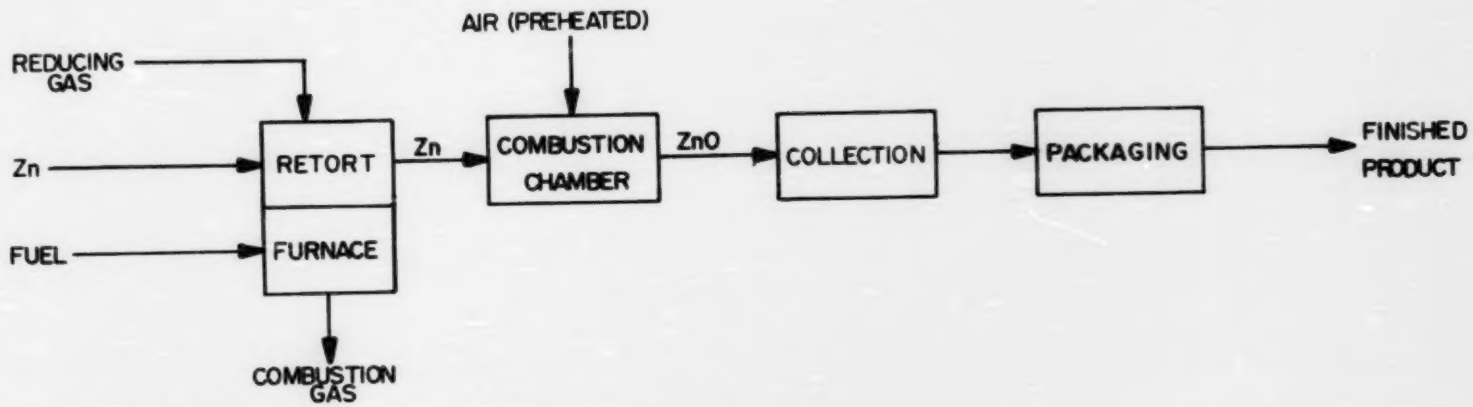

Figure 75. Flow Sheet For French Process

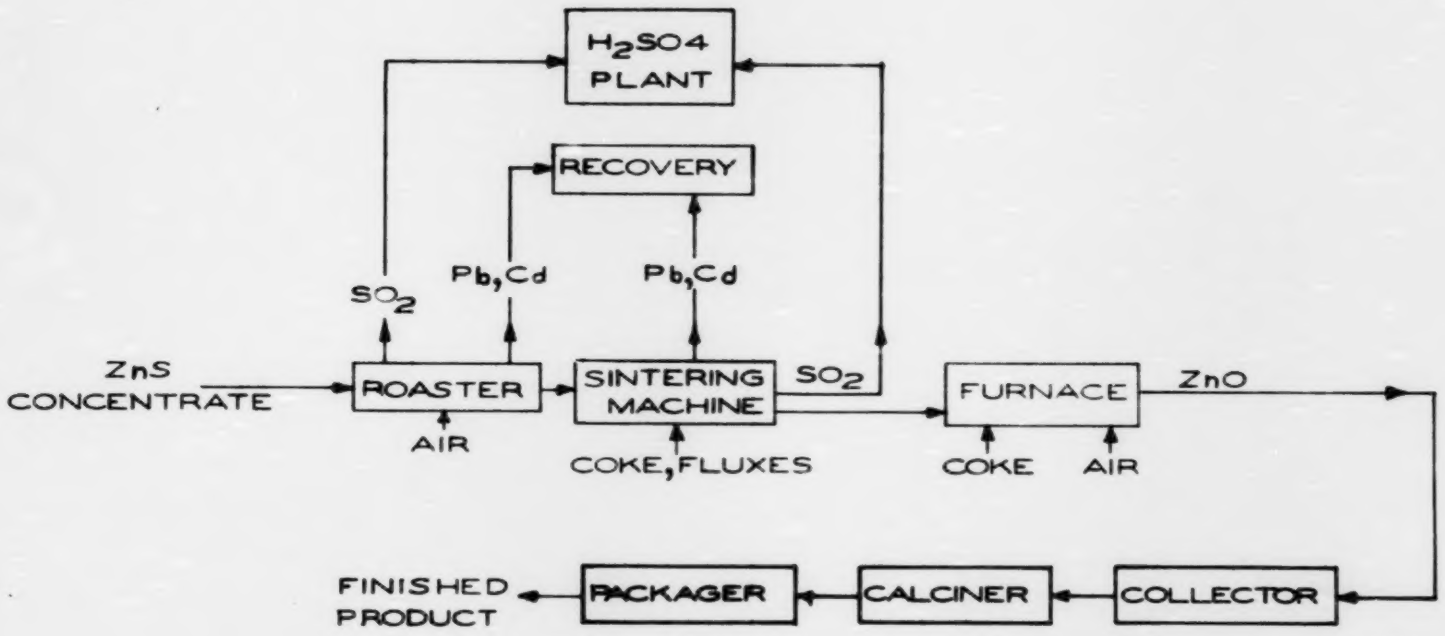

Figure 76: Flow sheet for American process

is then collected and packaged.

All of the above processes are presently in use. Most producers use both the French and American processes with a larger share of the production from the American. St. Joseph uses the electrothermal process exclusively. All of the producers except Eagle-Picher roast their own ore at the plant site. In the latter case, the ore is roasted at Blackwell, Oklahoma by AMAX and shipped to the zinc oxide plant. Where roasting is done, the SO_2 produced is used to manufacture sulfuric acid.

The characteristics of the three processes described are similar with respect to particulate emissions. The average particle size of ZnO produced is 0.2 to 0.25 microns. Some control of the particle size can be accomplished by a variation in the rate of oxidation, rate of cooling, air flow rate, etc. In this way, average particle sizes of 0.1 microns or less can be produced. Larger sizes of 0.4 microns and up can be produced by slow chilling or separate calcination of fine particles.

Product collection is achieved through the use of baghouse type filters. Collection efficiencies in excess of 99.9% (weight losses) are usually given for this type of collector. Very little hard data is available on efficiency, however, since designers tend to be more interested in such parameters as bag life, flow rate per square foot, etc. It must be kept in mind that extremely fine particles are involved here and this may affect efficiency. Eagle-Picher did some tests a few years ago and concluded that their filters operated at 99.9% efficiency. High efficiency in a baghouse is, of course, dependent upon proper mechanical operation and on the integrity of the bag filters.

Since almost all of the 220,000 ton/yr of zinc oxide is from only five producers, an average plant production of 44,000 ton/yr can be assumed. Assuming 99.9% collection efficiency this represents an emission of 44.0 ton/yr per plant, or about 0.12 ton per day per plant.

In addition to effluent through the baghouse filters, losses can occur in the handling and packaging operations. The amounts lost in this manner are largely a function of plant housekeeping and control. Product losses from this source should be confined to the plant site and probably do not significantly affect ambient air quality.

For the American and electrothermal processes additional particulate losses may occur in raw materials handling. These are estimated to be about 0.25 tons per 100 tons of zinc oxide produced.

The gas phase effluent from the zinc sulfide roaster contains SO_2, and some lead and cadmium, probably in the form of oxide particles, as well as smaller amounts of zinc. The metals are recovered in a cadmium recovery plant. The sulfur dioxide is fed to a sulfuric acid plant. The emissions characteristics of these materials, then, are those characteristic of sulfuric acid manufacture and cadmium recovery. Roasting of zinc ores is being examined in detail in a separate EPA study of smelters.

Most of the remaining SO_2, cadmium and lead are volatilized in the sintering and calcining steps. The vapors are fed to the acid plant and cadmium recovery units. In addition, small amounts of chloride compounds from any fluxes used in sintering are released in these steps.

Each of the three processes includes a furnace, or burner, in which the zinc oxide is produced. In the case of the American and Electrothermal processes a reduction of the crude ZnO also takes place and is included in the description of this operation. All of the effluent gases from these operations eventually pass through the baghouse filters discussed previously.

In addition to particulate materials there exist other potential sources of gas phase pollutants from the furnace. These come from the fuels and reducing agents used. For the American process, coal is charged to the furnace in the ratio of two tons of roasted ore per ton of coal. In the French process, vaporization of zinc metal takes place under a reducing atmosphere produced by the incomplete combustion of about 0.7 ton of coal per ton of ZnO product. The quality of the coal used in these operations can affect emissions with respect to the oxides of sulfur and nitrogen. The coke used in the Electrothermal process should be relatively free of these contaminants.

There exists, also, some possibility of CO emissions. Carbon monoxide is part of the zinc vapor stream leaving the furnace. This is burned in an excess of air which should minimize the amount of CO leaving the burner. This is confirmed by field experience.

Process heat for the retort in the French process and, perhaps, for air preheating in all the processes is supplied by burning either coal, gas or oil. The combustion gases are released directly to the atmosphere and present a potential source of emissions. The extent of emissions depends on the quality of the fuels used.

There are five major producers of zinc oxide as shown in Table 107. Two of these facilities (Eagle-Picher and American Smelting & Refining) are devoted solely to zinc oxide production. The other two companies also produce zinc metal at the same locations. All of the producers except Eagle-Picher roast their own sulfide ores. Approximately 50% of New Jersey Zinc's production by the American process starts with franklinite and so does not require a roasting step.

TABLE 107

ZINC OXIDE PRODUCERS

Producer	Location	Types of Processes	Production (ton/yr.)
Eagle-Picher	Hillsboro, Illinois	French, American	20,000
St. Joseph Minerals	Monaca, Pennsylvania	Electrothermal	N.A.
American Smelting & Refining	Columbus, Ohio	French, American	N.A.
New Jersey Zinc	Palmerton, Pennsylvania	French American	37,500 55,000
Sherwin-Williams	Coffeyville, Kansas	Modified American	20.000

C. Chrome Pigments[2,30]

The term "chrome pigment" includes a variety of compounds containing the chromate group, CrO_4^{2-}, or chromium oxide. The chromates of lead and zinc are used as pigments alone or in combinations with materials such as lead molybdate, $PbMoO_4$. The colors available with chrome pigments range from green to yellow to red. Consumption of chrome pigments in 1970 is estimated at 65,000 tons.[3] The most recent year for which production by types is available is 1968:[3]

Type	Formula	Production ton/yr
Chrome green	$PbCrO_4$ + Prussian Blue	2,830
Chromium oxide green	Cr_2O_3	6,230
Lead chromate yellow	$PbCrO_4$	32,790
Molybdate orange	$PbCrO_4 + PbMoO_4$	11,380
Zinc chromate	$ZnCrO_4$	7,400

Chromate compounds are considered toxic. Lead chromes have additional toxicity potential due to the presence of lead. In both cases they are not considered as hazardous as the white lead pigments.

Paint industry projections predict a 12% decrease in the use of the lead chrome yellow by 1975 and slight increases for the other chrome pigments.[31] The possible introduction of more stringent regulations with respect to lead content in paint could affect this picture considerably, however.

1. Lead Chromes — A variety of reaction schemes, all involving precipitation, are used in the production of lead chromates. Precipitation time, concentration of solution, pH and temperature and other reaction parameters influence the properties of the final product. The color depends primarily on the crystalline form of the $PbCrO_4$. The lemon yellow rhombic form, usually the desired product, readily converts to the stable, reddish monoclinic form. Various techniques, such as co-precipitation with lead sulfate, have been found which largely stabilize the rhombic form. Another stability problem is the photochemical conversion of adsorbed soluble lead salts to metallic lead and/or the lower oxides of lead, which causes a darkening of the paint film. Methods are available to partially, though not completely, overcome this problem.

Four commonly used reaction schemes are illustrated below:

$$Pb(NO_3)_2 + Na_2CrO_4 \rightarrow PbCrO_4 + 2NaNO_3 \qquad (1)$$

$$2Pb(NO_3)_2 + Na_2Cr_2O_7 + 2NaOH \rightarrow 2PbCrO_4 + 4NaNO_3 + H_2O \qquad (2)$$

$$Pb(acetate)_2 + Na_2CrO_4 \rightarrow PbCrO_4 + 2Na(acetate) \qquad (3)$$

$$PbO + 2HNO_3 + Na_2CrO_7 \rightarrow 2PbCrO_4 + 2NaNO_3 + H_2O \qquad (4)$$

Lighter shades are produced containing about 40% lead sulfate. Darker shades close to orange are produced by alkali treatment and contain up to 40% PbO.

2. Zinc Chromes — Pigmentary zinc chrome is most commonly a basic zinc potassium chromate, $K_2CrO_4 \cdot 4Zn(OH)_2$. Zinc tetroxychromate, $ZnCrO_4 \cdot 4Zn(OH)_2$ is also coming into prominence. These pigments are lemon yellow in color and have some useful properties, though they are inferior to lead chromes in opacity and in staining power. Their main use is the manufacture of anti-corrosive coatings. Both pigments are produced by precipitation from aquous suspensions of zinc oxide. Two methods are used in the production of basic zinc potassium chromate:

$$4ZnO + 2CrO_3 + K_2Cr_2O_7 + H_2O \rightarrow \text{product} \qquad (1)$$

$$4ZnO + 2K_2Cr_2O_7 + H_2SO_4 \rightarrow \text{product} + K_2SO_4 \qquad (2)$$

Zinc tetroxychromate is produced from zinc oxide and chromic acid as follows:

$$5ZnO + CrO_3 + 4H_2O \rightarrow ZnCrO_4 \cdot 4Zn(OH)_2$$

3. Chrome Green — Lead chrome greens are produced by mechanical mixture of lead chromes and prussian blue, $KFe \cdot Fe(CN)_6 \cdot xH_2O$, or by precipitation of lead chromes in the presence of prussian blue. Manufacture of these pigments represents an extreme fire hazard, since prussian blue is combustible and lead chrome will act as a source of oxygen. This enables chrome green to burn independently of an external source of oxygen. Large volumes of ammonia are produced during combustion.

4. Chromium Oxide Greens — This pigment consists of pure chromic oxide, Cr_2O_3. It is prepared by burning a mixture of sodium dichromate and sulfur. About 30 to 40% excess sulfur is used. The reaction is indicated by the following equation:

$$Na_2 Cr_2O_7 + S \rightarrow Na_2SO_4 + Cr_2O_3$$

The excess sulfur is largely evolved as SO_2. Small amounts of SO_3 might also be present since Cr_2O_3 is known to catalyze the oxidation of SO_2 somewhat.

Chromium oxide greens have exceptional chemical, light and thermal stability. Its color, unfortunately, is considered rather unattractive and this limits its use. It is confined largely to applications where durability is more important than appearance. It finds considerable military use since its infrared reflectance spectrum approximates that of natural foliage.

5. Molybdate Orange — Molybdate oranges are produced by coprecipitation of lead chromate, lead sulfate and lead molybdate to produce a mixed crystal $PbCrO_4 \cdot PbSO_4 \cdot PbMoO_4$. This

forms a fairly stable system ranging in color from orange to scarlet. It is often used in combination with organic reds and maroons to produce a variety of shades.

As a general group, chrome pigment ranks second among the inorganic color pigments in total tons produced for the paint industry. Of the five major types of chrome pigments produced, four are made via wet chemistry and offer no significant air pollution emission. The fifth, Cr_2O_3, is the only pigment that emits a significant air pollutant. The production of this pigment is only 10% of the total chrome pigment production and its use has been declining. As outlined earlier, it is produced by reaction with elemental sulfur. Assuming a maximum of 40% excess sulfur is required in the production, an emission of 1,050 tons/year of SO_2 can be calculated from the yearly production of 6,230 tons/year of chromic oxide. Current technology for control of SO_2 is well developed and requires no further discussion in this report, and it is sufficient to say that this emission can be easily controlled.

It is also anticipated that the use of the leaded chrome pigment will also be declining in the future by restriction of the lead content of paint. This decline has been reflected by the National Paint & Coating Association's "Raw Materials Usage Survey" for the year 1970. They project, for example, a drop of consumption of chrome yellow pigment of 9% for the year 1972. This is not as severe as the 50% drop projected for lead oxide pigments over the same period; but people in the industry are not as yet certain how the new ban on lead contents will be applied. It is fair to assume, however, that the lead ban on paints will reduce the usage of leaded chrome pigment significantly. This fact coupled with the earlier discussion eliminates these pigments from more detailed study.

D. Iron Oxides[2,30]

Iron oxide pigments as a group represent the most widely used color pigments in the coatings industry. The estimated consumption of these pigments in 1970 stands at 142,500 tons.[3] This represents an amount exceeding the consumption of all other inorganic color pigments combined. The popularity of iron oxide pigments can be attributed to their low cost, good physical and chemical properties and the range of colors available. Iron oxide is non-toxic.

Iron oxide pigments may be broadly classified as either natural or synthetic. About 53% of 1968 consumption consisted of synthetic oxide.[35] Paint industry projections predict only a small increase in the use of the natural material. An increase in the use of synthetic iron oxide of from 25% to 42%, depending on the type, is projected between 1970 and 1975.[31]

The color depends on the type of iron compound. Red pigments are essentially ferric oxide, Fe_2O_3. The yellows are hydrated ferric oxide, $Fe_2O_3 \cdot H_2O$. Black pigments are a ferrosoferric oxide, Fe_3O_4. The browns are a mixture of the above types.

The production of natural iron oxide pigments starts with the mining of iron oxide. Iron ore deposits are available in various parts of the world which are suitable for use in pigments. Their chief advantage is low cost. Their disadvantages include non-uniformity, lack of color purity and presence of impurities which may influence their properties to a greater or lesser extent depending on the application.

These pigments are produced using various combinations of some or all of the following four operations.

1. Drying. The material is dried at about 120°C to remove unbound water.
2. Grinding, either wet or dry, to a maximum size of about 15 microns, or less.
3. Wash and Purify. The material may be washed several times in the course of processing. Purification can take place by wet or dry classification, settling, etc.
4. Calcining. The material can be calcined at 400 to 500°C to remove hydrated water or increase the degree of oxidation. In this way, the yellow oxide can be converted to red, if desired.

The production of synthetic iron oxides represents more complex chemical and physical operations than those used in the preparation of natural pigments. The starting materials are usually ferrous chloride (pickle liquor from iron steel manufacture) or ferrous sulfate (copperas, from sulfate process TiO_2 production).

Yellow iron oxides, ranging in color from light lemon to deep orange, are produced by the following steps:

1. Precipitate ferrous hydroxide, $Fe(OH)_2$, by the addition of alkali. The precipitate forms a suspension.
2. Blow air at a controlled temperature through the suspension to form geothite, $-FeO \cdot OH$, "seed" crystals.
3. Provide an additional source of ferrous ion and continue to blow air through the suspension. One way this is accomplished is to introduce scrap iron into the tank. As the ferrous ion is oxidized, hydrogen ions are formed which simultaneously react with the iron to form additional ferrous. The reaction scheme may be represented by:

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4FeO \cdot OH + 8H^+$$

$$8H^+ + 4Fe \rightarrow 4Fe^{2+} + 4H_2$$

$$\overline{4Fe + O_2 + 6H_2O \rightarrow 4FeO \cdot OH + 4H_2}$$

The newly formed oxide is deposited on the "seed" crystals causing them to grow until the desired size is reached.

4. Wash, filter, and dry.

Paint industry projections predict a 42% increase in the consumption of synthetic red iron oxide pigments between 1970 and 1975. Production of synthetic reds in 1968 was 34,342 tons.[35] This figure does not necessarily reflect production for uses other than as pigments. Particle sizes often encountered with red iron oxides range from 0.2 to 0.8 microns. There are three principal methods used in manufacturing these pigments.

Copperas reds are produced by calcining ferrous sulfate at a temperature sufficiently high to cause decomposition to ferric oxide, Fe_2O_3. The ferrous sulfate is first subjected to a mild calcination to remove hydrated water. This is followed by a severe calcination in air to cause decomposition. The reaction may be represented by the following equation:

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

This reaction has a dissociation pressure of 546 mm at 654°C. Copperas reds are considered the most important group. They accounted for 18,910 tons production in 1968.[35]

Ferrite reds are produced by the dehydration of yellow ferric oxide. If calcined at 400 to 600°C, "Turkey Reds" are produced. If calcined at upwards of 900°C, "Indian Reds" result.

Precipitated reds are produced by precipitation from copperas or ferrous chloride solutions. The ferrous hydroxide is precipitated with caustic, aerated at 60 to 90°C, and then washed, filtered and dried. No calcining is involved. This produces a pigment free of aggregates and quite uniform in size.

A fourth type of red is made in very small amounts. This is Venetian Red made by precipitating copperas with lime, aeration and calcination to produce a pigment containing 40% Fe_2O_3 and 60% $CaSO_4$.

Brown iron oxide pigments can be made by blending the pure reds, yellows and blacks or by precipitation and calcination. Blacks are produced by complete precipitation from copperas or ferrous chloride followed by aeration at the boiling point of the solution. 6,177 tons of brown and 3,560 tons of black iron oxides were manufactured in 1968.[35]

With one exception, all of the processes used for manufacturing iron oxide pigments should be relatively free of atmospheric emission problems. Most of the operations are aqueous in nature and do not produce gas phase pollutants. Since the fine particles of dry pigment eventually produced represent product, it would be expected that particulate emissions would be well controlled. Adequate methods are available for highly efficient collection of fine particulate.

The one process which can produce serious problems is the manufacture of copperas reds. Here the production of large volumes of SO_2 and SO_3 must be contended with. The production of 18,910 tons of copperas red causes the release of 7,600 tons of SO_2 and 9,500 tons of SO_3. This must be recovered as sulfuric acid or otherwise accounted for.

There are two major producers of synthetic iron oxide pigments along with a number of smaller manufacturers. The largest producer is Cities Service, Inc. with a plant producing precipitated yellows and reds at St. Louis, Missouri and another producing synthetic reds at Monmouth Junction, New Jersey. The second major producer is Pfizer Minerals with plants at East St. Louis, Illinois, Easton, Pennsylvania and Emeryville, California. The plants at East St. Louis and Easton produce calcined copperas.

The smaller producers include Reichard-Coulston, Bethlehem, Pennsylvania. Their production includes calcined copperas. They report that they have a scrubber of unspecified type on their copperas calciner.

Mineral Pigments Corporation at the present time does not manufacture red iron oxide and deals primarily in natural materials. Chemtron and Hilton-Davis both produce a line of transparent iron oxides for the specialty market, primarily automotive finishes. These are made by precipitation processes followed by mild calcining to remove water.

E. Titanium Dioxide Pigments[3,36]

Titanium dioxide is an opaque, white material. When used as a pigment in the paint and lacquers, it provides excellent hiding power due to the very high refractive index of the two crystalline forms, rutile and anatase. This excellent hiding power and lack of toxicity combine to make titanium dioxide the leading hiding pigment in the paint industry, measured by either tonnage of material consumed or dollar value.

Two processes are used for the production of titanium dioxide pigments. These are the sulfate process and the chloride process. These processes use several titanium-bearing raw materials. The principal sources of these are:

1. Ilmenite, or iron titanate, which is mined in the U.S., as well as several foreign countries.

2. Slag from the electric-furnace smelting of ilmenite which yields a salable iron product and a high — TiO_2 content slag.
3. Rutile, which occurs naturally in Africa, Australia, and several other countries outside the U.S.
4. Leucoxene, a highly-weathered ilmenite possibly supplemented with minor amounts of ilmenite containing 70 to 80% TiO_2.

The sulfate process is the oldest and most versatile of the two processes. It may use ilmenite or slag, and is capable of producing either rutile or anatase. The chloride process produces equivalent products. The details of chloride process technology are often considered proprietary by the industry and it is difficult to define the state of the art. Historically, the chloride process has produced rutile pigment only and has required rutile ore as raw material. Currently, however, techniques have been developed which permit use of ilmenite ore (possibly upgraded). Also, it is now possible to produce anatase TiO_2 by the chloride process.

This discussion is concerned principally with the manufacturing process for titanium dioxide as they relate to atmospheric emissions. Much of the information available relating to the economics of the application of the two principal pigment types and the many variables with regard to particle size, surface chemistry, etc., will be omitted from the discussion if they do not have a particular bearing on the emission-related characteristics of the process. On the other hand, those details of the manufacturing process and properties of the materials which do relate to variations in atmospheric emissions from one plant to another or within a given plant, will be included.

Of particular interest in the consideration of the process in the following paragraphs is the fact that there is a limited number of producers of titanium dioxide in the U.S. Each of these practices the processes described in ways that incorporate some characteristics peculiar to that manufacturer. This discussion will not identify all of the processing variations and relate them to specific manufacturers. However, those which are important to the atmospheric emission aspects of the process have been characterized insofar as possible, with respect to the particular manufacturer. Those companies known to be engaged in the production of titanium dioxide within the U.S. at this time are tabulated on the following page.

Manufacturing Company	Sulfate Processing	Chloride Processing
American Cyanamid	Yes	Yes
Kerr-McGee	No	Yes
Cabot Corporation	No	Yes*
DuPont	Yes**	Yes
New Jersey Zinc	Yes	Yes*
NL Industries	Yes	No
SCM Glidden	Yes	Yes
Sherwin-Williams	No	Yes

1. Sulfate Process — The most common raw material for the sulfate process is ilmenite. The principal constituent of ilmenite is iron titanate, $FeO \cdot TiO_2$. This is found associated with various minerals, such as vanadia, alumina, etc. Table 108 gives the chemical composition of several of the ores with each of the elements reported as its oxide form. In addition to the common ilmenite, found in the U.S., in the Adirondacks and in Florida, and in Australia and Canada, a co-product slag produced by the smelting of Canadian deposits is a frequent raw material for titania manufacture in the U.S.

In the sulfate process, the iron titanate is dissolved in concentrated (66° Baume) sulfuric acid to yield titanyl sulfate, ferric sulfate, ferrous sulfate and other soluble mineral sulfates and gangue residue. The principal reaction, greatly simplified, for this digestion is:

$$FeO \cdot TiO_2 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

This reaction is carried out batch-wise in multiple digesters which feed a semi-continuous process. The solid sulfate cake is dissolved in water and recirculated acid to yield "sulfate solution". The immediate objective is to put as much of the titanium into solution as possible. At this point, it is objectionable to have metals of high valence present in the solution and the solution is treated with a reducing agent such as metallic iron to bring about reduction of ferric ions and other metal impurities to a low valence state. The typical reduction reaction taking place in the digester is:

$$Fe^0 + 2Fe^{+++} \rightarrow 3Fe^{++}$$

After digestion, all of the insoluble metallic components are filtered and removed from the solution. All of the iron remains in solution at this point.

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*N.J. Zinc has recently been reported to have leased the chloride production facilities of the Cabot Corporation.

**Will be discontinued by the end of 1974.

TABLE 108

ANALYSIS OF ILMENITE ORES

	United States					Canada		
	Virginia							
Chemical Constituent	Piney River	Roseland	New York	Florida	California	Ivry	Bourget	Allard
TiO_2	44.3	51.4	44.4	64.1	48.2	42.5	22.4	37.3
FeO	35.9	37.9	36.7	4.7	39.1	39.1	36.9	26.3
Fe_2O_3	13.8	1.6	4.4	25.6	10.4	20.7	31.2	30.0
SiO_2	2.0	4.6	3.2	0.3	1.4	0.88	1.0	
Al_2O_3	1.21	0.55	0.19	1.5	0.2	1.05	6.01	
P_2O_5	1.01	0.17	0.07	0.21			0.93	0.004
ZrO_2	0.55		0.006		0.05			
MgO	0.07	2.35	0.80	0.35	0.6	2.0	1.50	
MnO	0.52	0.70	0.35	1.35	0.1	0.04		0.10
CaO	0.15	0.59	1.0	0.13	0.1	0.1	0.55	
V_2O_5	0.16	0.07	0.24	0.13	0.05	0.36		0.39
Cr_2O_3	0.27		0.001	0.1	0.03	0.15		

When ilmenite is used, the next processing step consists of cooling the solution to crystallize out some of the iron as $FeSO_4—7H_2O$. The next processing step involves the dilution and heating of the sulfate liquor, which hydrolyzes the titanyl sulfate and brings about precipitation of titania. The basic chemical equation for this hydrolysis step is:

$$TiOSO_4 + H_2O \rightarrow TiO_2 + H_2SO_4$$

During subsequent processing, the titania is present as a precipitate, and most of the impurities remain in solution. Several filtering and washing steps follow, in each of which the titania is retained on the filter, and the filtrate and wash water are recycled or discarded. Although the basic TiO_2 material is formed during the hydrolysis step, the product of this part of the reaction is a fine, non-pigmentary material.

Subsequent processing steps are aimed at modifying the particle size and crystallinity, conditioning the surface of the particles and performing other proprietary treatment steps to produce a final pigment material with the desired properties. The next step in the preparation of the finished pigment is calcination.

In a rotary calciner, the TiO_2 "hydrate" cake is dried and calcined to achieve the final crystalline product. Here, no basic chemical change takes place, but the recrystallization of the titania to form either anatase or rutile crystals of the desired size, is accomplished.

Following calcination, the crystallites are milled and packaged for shipment. Alternatively, the particles may be treated with various surface-coating agents to achieve particular properties of dispersibility, resistance to weathering, etc.

Figure 77 contains a detailed process flow diagram for the manufacture of either rutile or anatase from ilmenite by the sulfate process. Some of the processing steps in this process are carried out batch-wise, while others are continuous. Similarly, some of the emission sources produce variable rates and compositions of air pollutants while others are relatively steady and continuous.

The ilmenite ore* is a black, powdery material of relatively coarse particle size, which produces some dusting as it is transferred from rail car, ship or truck to an ore holding yard to await processing. Again, some dusting may occur as the ore is loaded onto belt or bucket conveyors for transfer to the ilmenite dryer, which forms the first step in the manufacturing process.

The ilmenite is dried in a counter-current gas or oil-fired dryer. The dryer is generally equipped with a mechanical dust collector, fabric collector or electrostatic precipitator at the gas discharge end. Dust captured by the collector is returned directly to the process. Because of the

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*It will be understood that in the following discussion, the term "ilmenite" is meant to include, also, high TiO_2 slag.

FIGURE 77A
TiO2 MANUFACTURE SULFATE PROCESS

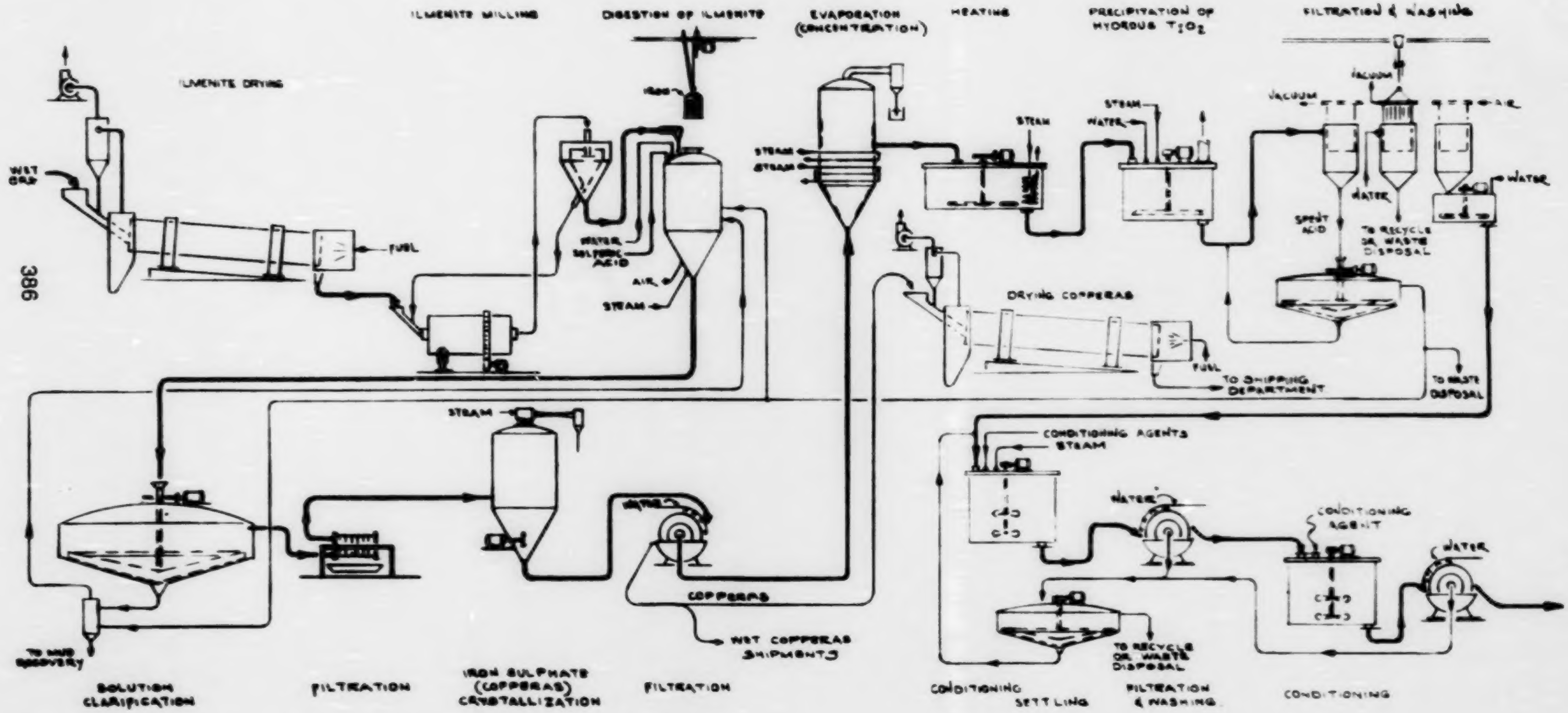
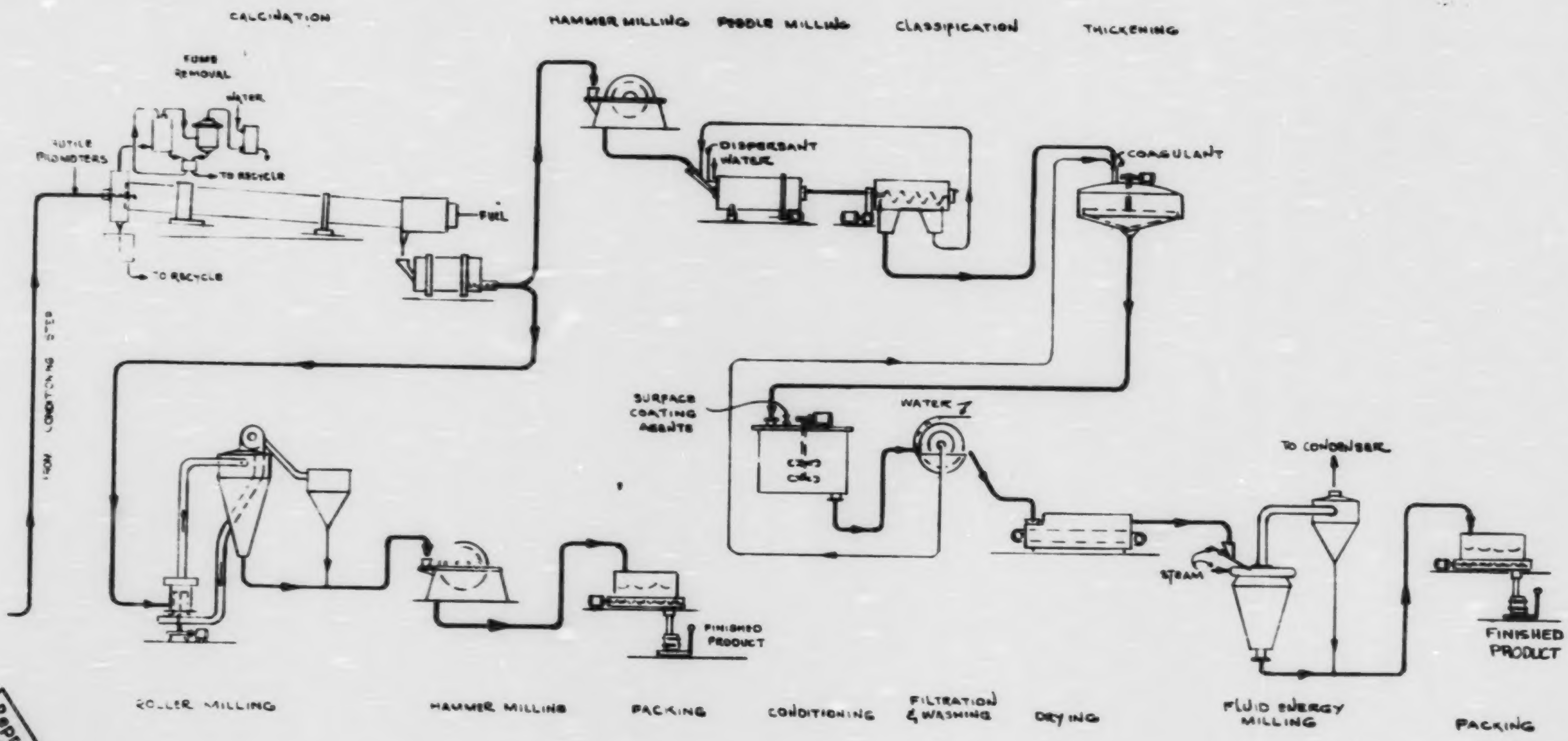


FIGURE 77B
TiO_2 MANUFACTURE SULFATE PROCESS



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relatively coarse size of the raw ilmenite, there is little net loss of dust from the drier. Sulfur dioxide may be present as a gaseous emission if fuel oil is used rather than natural gas. The drier ordinarily runs continuously and feeds dry ilmenite ore to a ball or pebble mill for grinding.

The rotary mill operates without any gas source, and is relatively free of a dusting problem. Following the mill, the ground ore passes through a classifier which separates oversized particles for return to the mill and passes particles of sufficient fineness to one of the batch digesters. Here again, there is no gas emission from the classifier and therefore, little likelihood of emission of dust or fumes, although electrostatic precipitators may be used on some milling systems.

The digesters are charged sequentially with dry, milled ilmenite ore. During charging, there may be some dust emission through the ventilating stack on each of the digesters. Charging is complete in a matter of a few minutes, and the dust emission ceases when the ore has become wetted with the sulfuric acid added to the digester.

The initial digestion reaction starts relatively slowly, with the reaction mass at a temperature slightly above ambient temperature. Steam is added to increase the temperature and the reaction rate, and air sparging for agitation may be used. As the exothermic reaction proceeds, the temperature of the reaction mass increases and the rate of reaction increases. After approximately 5 to 30 minutes, the reaction rate reaches a peak for about 10 to 15 minutes and the maximum rate of emission of steam, sulfuric acid mist, particulate matter and sulfur dioxide through the stack occurs. Subsequently, the reaction slows down, but steam emission continues until the reaction mass has "set" to form a solid.

After the digestion reaction is complete, water and possibly some recirculated acid, is added to the digester to dissolve the solid. At this point in the cycle, scrap iron in a basket-like container is immersed in the solution and allowed to remain in contact with the solution until the reduction of ferric ions to ferrous and some slight reduction of titanyl sulfate has taken place. Other reduction techniques may be used in some plants. When the desired degree of reduction is achieved, the sulfate solution is transferred to a clarifier.

The clarifier is basically a large settling tank in which a rotating rake processes settled material toward the center for removal as a solid "mud". Although the digesters discharge intermittently, the clarification tanks operate on a continuous basis. In the clarification process, proprietary floculating and coagulating agents may be used to improve sedimentation of the solid impurities. In some cases, hydrogen sulfide or other chemical reagents may be added to aid in the floculation and removal of solids. It is customary to use completely closed clarifier vessels, even if hydrogen sulfide or other gaseous reagents are not used. Typically, the clarifiers operate at 60 to 80°C and some evolution of water vapor is normal. The mud collected at the bottom of the clarifier is washed with recycled sulfuric acid to remove any dissolved titania and the acid from this washing is returned to the digester. The mud is disposed of by landfill, by sluicing or may be used as a source of minerals in a recovery process.

The clarified sulfate solution may be passed through a filter process to remove the last traces of solid material and then passed into an iron sulfate cyrstallizer. This is simply a closed vessel which is evacuated through a steam jet ejector to a barometric condenser. The pressure reduction brings about evaporation of water from the sulfate solution which cools the solution and concentrates it with respect to both titanium sulfate and iron sulfate. The objective of this step is to crystallize some of the iron sulfate for removal from the process.* The crystallization takes place in multiple-batch vessels which are mechanically agitated as the cooling, evaporation and crystallization take place. After sufficient water has been removed, the slurry of iron sulfate-titanium sulfate solution is passed through a drum filter where the ferrous sulfate solid is removed. This solid product consists almost completely of $FeSO_4 \cdot 7H_2O$, and is normally called "copperas". Copperas is not produced when slag is the principal raw material.

Copperas is the principal raw material used in the manufacture of iron oxide pigments, and certain other iron containing pigments. It is fairly common for a plant preparing iron pigments to be located nearby and to use the wet copperas filter cake, as it comes off the filter press, for raw material. In some cases, the use of the copperas is restricted to plants located at some distance from the titanium oxide plant. When this is the case, the filter cake is conveyed to a rotary drier and copperas is dried for bulk shipment to distant points. Where a drier is used, it is necessary to provide a mechanical dust collector and possibly a fabric collector on the flue gas discharged from the drier.

The filtrate from the copperas filter is conducted to evaporation and concentration vessels in which further concentration of the titanium sulfate solution takes place batch-wise. This vessel is provided with steam heat coils and operates under vacuum provided by a barometric condenser. This concentration step increases the titanium concentration to the equivalent of about 200 grams (measured as TiO_2) per liter of solution.

Further heating is accomplished in a separate stirring-heating vessel using steam coils as the heating source. After this heating step, the strong solution is diluted and additional heating brings about hydrolysis of the titanyl sulfate to hydrated titanium dioxide. It is in this step that the predominant color of the titanium compounds changes. In all prior steps, the predominant color of the solution and slurry materials is the black of the ilmenite and the sulfate solutions. In the hydrolysis step, the white color associated with titanium dioxide pigment develops. From this point forward in the processing, the processing equipment is referred to as the "white end" of the plant.

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*Normally, crystallization is not done when processing slag solutions.

After boiling from 3 to 6 hours in the hydrolysis reactor, the slurry is transferred to filters in which the precipitated titania is separated as a solid product and the filtrate is circulated to a closed spent-acid clarifier. The overflow from this clarifier is partially recycled to the digestion process and to the mud washing step, and the remainder to disposal. The underflow contains some titania which passed through the filters. This sludge is recycled to the filters for recovery. The solid titania removed from the leaf filters is reslurried with water and transferred to a bleaching reactor. In this step, conditioning agents, dilute acid and materials such as aluminum or zinc are added to bring about a slight reduction in the titania and produce the optimum brightness. The material leaving the conditioner is filtered and dilute acid filtrate recycled through a slurry settler. Overflow from the dilute acid settler is recycled or discarded while the solids are recycled to the bleaching step. The titania hydrate retained by the filter is washed on the filter and transferred to a second conditioning step. Here, proprietary conditioning agents are added to modify the crystalline structure and improve the properties of the final pigment. For example, antimony may be added at this step to modify the chalking properties of the titanium pigment.

The slurry is again filtered, with washing of the filter cake on the drum, and recycle of the dilute acid filtrate into the dilute acid settler. The washed solid material is discharged into the calciner.

Catalysts for promotion of rutile formation may be added at the calciner inlet if rutile is the desired end product.

Calcination comprises a critical step in the pigment processing in that it is in the calciner that the final crystalline form is established as either anatase or rutile. Also, the gaseous discharge from the calcination step comprises one of the largest and most difficult single emission sources in the manufacture of titanium pigments.

The calcination step involves the removal of water of hydration from the titanium slurry, and, subsequently, crystallation of the titanium dioxide. During the first half of the calcination process, water alone is removed from the solids being transported through the rotary calciner. As the temperature reaches 200°C or so, water evaporation is complete and sulfuric acid vapor is released from the solid. The temperature continues to increase as the solid passes through the calciner toward the firing end and temperatures of 900°C or so are reached at the discharge end.

The equilibrium product from the calciner is the rutile form of TiO_2. However, the anatase form tends to be produced as an intermediate, and severe calcination conditions, that is, high temperature and long residence time, are required to produce recrystallization to the rutile form. It has been found that the formation of rutile is promoted by the addition of catalytic materials. These are used as "rutile promoters" if rutile is the preferred product.

The calciner is generally fired with natural gas or oil. In addition to the products of combustion, sulfuric acid vapor driven from the titania is released into the gas stream, and this partially decomposes to produce SO_3 and small amounts of SO_2 by decomposition of the sulfuric acid. In addition, there may be some entrainment of the titanium dioxide at the feed end, although this is nominal because of the large size of agglomerate particles and the relatively high moisture content at the feed end of the calciner.

The treatment of the flue gas discharge from the calciner varies from plant to plant. One of the common combinations of processing steps is shown in Figure 77. This involves water quenching of the flue gas to reduce the temperature to well below the condensation temperature of sulfuric acid mist (below 240°F or so) and provides an initial water wash step. Effluent from the cooler-condenser then passes upflow through a tubular electrostatic precipitator. Lead is the preferred material of construction for ductwork, precipitator tubes and housing. The discharge from the electrostatic precipitator then passes through a final scrubber, constructed of redwood. Condensate from the precipitator as well as the water from the initial quenching step is recycled to various parts of the process.

In the final washer, large volumes of water are used on a once-through basis and achieve substantial reductions in sulfur dioxide concentration in the gas. This water is ordinarily discarded after use in the scrubber.

An alternative processing scheme utilizes a venturi scrubber with approximately 40 in. water column pressure drop across the throat to accomplish the sulfuric acid mist recovery in place of the electrostatic precipitator. This use of venturi scrubbers at this stage of the process must be considered experimental, as of this date, since fully satisfactory operation of such scrubbers has not yet been achieved.

The hot titanium dioxide leaving the discharge end of the calciner passes through a cooler and then into the final finishing line. Finishing may be accomplished by a sequence of wet finishing operations, or, alternatively, by dry finishing.

In the wet finishing scheme, the calcine passes in sequence through a Hammermill and rotary pebble or ball mill. Water is added in the Hammermill and all of the subsequent operations are carried out with the titania wet. Wet classification with recycle of oversized material to the pebble mill is followed by thickening of the slurry. The underflow from the thickener is treated in a conditioning reactor in which surface coating agents and other conditioners may be added to modify the properties of the titania. For example, aluminum hydroxide or silica may be added to alter the dispersion properties of the pigment, according to whether it is intended for dispersion in oil-based vehicles or in water.

After the final conditioning, the pigment is again filtered and washed on a rotary drum filter from which the filtrate is recycled to the final thickener. The filter cake is dried and discharged into a final milling step. This mill or "micronizer" deagglomerates the titania to produce the basic particle size set originally in the crystallization and calcining steps. The micronizer operates by subjecting the dried solid to extremely high velocity jets of steam. The stream leaving the micronizer is condensed and the finished dry product is packaged in bags or conveyed to bulk containers for bulk shipment.

The dry finishing alternate consists of roller milling and Hammermilling prior to packaging. The roller milling step involves the production of a substantial quantity of entrained titania dust which is collected in a large cyclone and a final fabric filter. The material collected from both of these recovery stages is passed on to the Hammermill, which produces the final particle size desired. Again, the final product may be bagged or prepared for bulk container shipment. Materials intended for water base paint applications or for use in paper manufacture may be reslurried for wet transport.

In a complex industrial process involving many stages, there are numerous potential sources of atmospheric emissions. Many of the potential sources relate to housekeeping and retention of product within the process rather than to necessary gas emissions into the atmosphere. In the production of titanium dioxide, many opportunities present themselves for loss of product as dry transfer operations and handling of the ilmenite ore, calcine or final product are carried out. In this discussion, only those sources which relate to necessary emissions of gas from the processing stages will be considered as legitimate potential air pollution emission sources.

The most significant of these legitimate sources involves the drying of the initial ore, digestion of the ore or slag and calcination of the titania after hydrolysis. In some of these, the gaseous emission consists principally of the products of combustion of the drier or calciner into which particulate matter is entrained. In addition, sulfuric acid and SO_2 are emitted by the calciner as the result of vaporization and decomposition of sulfuric acid from the titania hydrate calciner feed. In the case of the digester, the gaseous emission consists principally of steam produced by the vaporization of water as the digestion reaction is carried on. Each of these sources will be discussed in some detail in the following paragraphs. In addition, a number of secondary sources exist which involve limited discharge of gases into the atmosphere or from which the discharge is routinely and uniformly controlled in order to preserve the basic product. Examples of these secondary sources are:

Ore milling
Copperas drying
Final milling of pigment product.

2. Chloride Process — The chloride process for titanium dioxide pigment production is an alternative route to the manufacture of rutile pigments. The process is continuous to a higher degree than is the sulfate process, yields a pigment of lower impurity content which may be important in some applications, and, generally, has fewer sources of emissions requiring control. On the other side of the ledger, the chloride process has historically been limited in the range of raw materials which can be used to rutile or high - TiO_2 feed stocks. It involves corrosion, heat transfer and materials handling problems of unusual severity.

The fundamental chemical reactions involved consist of chlorination of titanium dioxide according to:

$$C + TiO_2 + 2Cl_2 \rightarrow TiCl_4 + CO_2$$

$$\text{and } 2C + TiO_2 + 2Cl_2 \rightarrow TiCl_4 + 2CO$$

After chlorination, the liquid titanium tetrachloride is purified by various solids removal, chemical treatment and distillation procedures and is then oxidized according to:

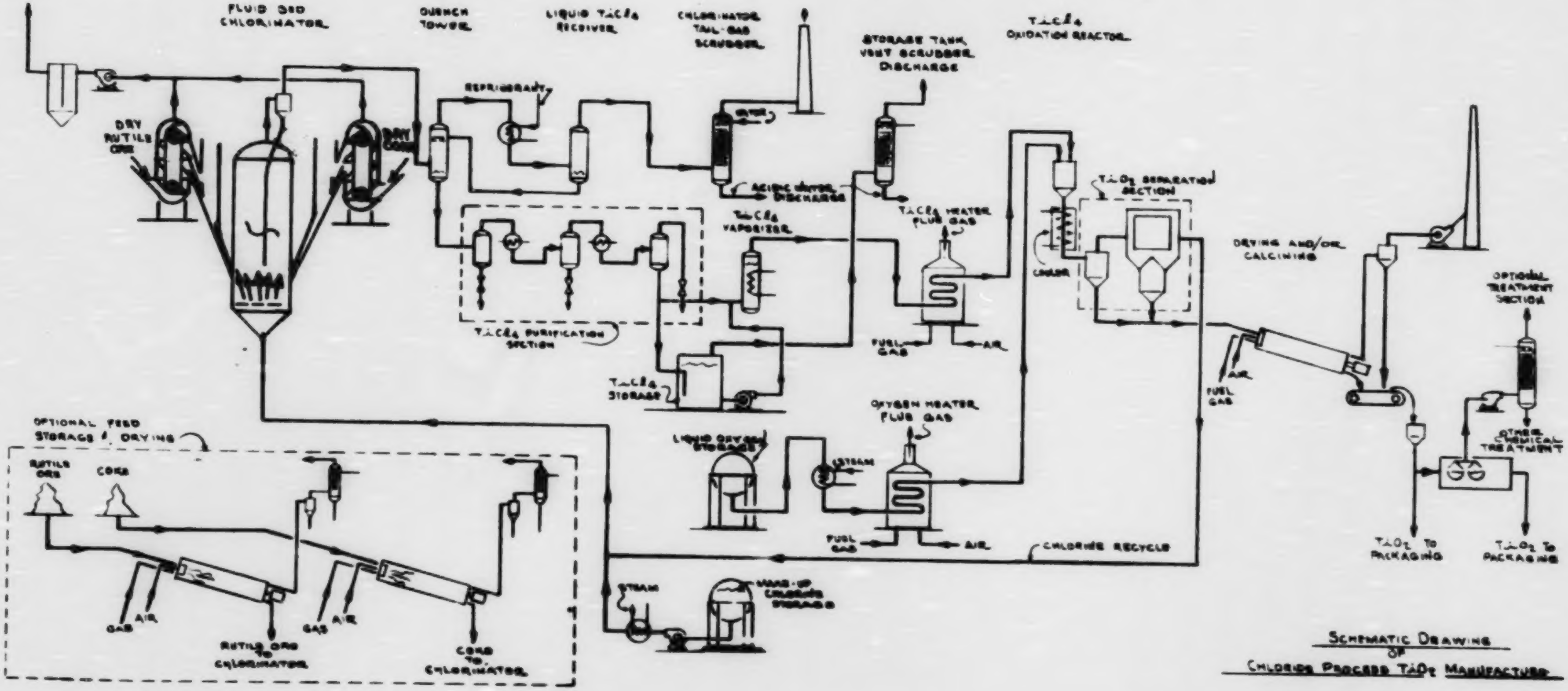
$$TiCl_4 + O_2 \rightarrow 2Cl_2 + TiO_2$$

These simple equations do not, of course, express the complexity of, nor sophistication required for, the manufacture of TiO_2 by the chloride process.

The basic flow scheme is illustrated in Figure 78. Ore, or combinations of ore and slag, are charged into a continuous chlorinator along with coke. The TiO_2 bearing ore and the coke are frequently shipped by rail or ocean-going vessels and unloaded for storage in open areas.

FIGURE 78

TiO_2 MANUFACTURE CHLORIDE PROCESS



The moisture content of both coke and ore stored outside is likely to become too high for use in the chlorinator, unless it is dried in gas-fired rotary driers as shown in the box in the lower left hand corner of Figure 78. If these driers are used, the dust generated in handling is a potential source of pollution, and the flue gases must be treated by mechanical collectors, fabric filters or other particulate abatement device prior to discharge into the atmosphere.

In some cases, it is possible to arrange for unloading and storage of the ore in enclosed buildings or sheds. This prevents the accumulation of excessive moisture contents in either raw material, and obviates the need for drying.

In either case, some dusting of the dry ore and coke in the handling process involved in removing them from storage and elevating them to the reactor level is unavoidable. It is customary to ventilate the conveyors, elevators, etc., through a fabric collector, or other high-efficiency particulate control device. Figure 78 shows a pressurized fabric collector on the ventilating air drawn from two bucket elevators.

The coke serves as a reducing agent and receptor for the oxygen liberated during chlorination of the titanium ore. Gaseous chlorine is fed into the reactor and carbon dioxide, carbon monoxide and titanium tetrachloride vapor are the principal products. Substantially all of the chlorine and all of the coke are used up in the chlorination process. Following condensation to remove titanium tetrachloride, gases vented from the chlorination reactor consist principally of carbon monoxide and carbon dioxide and other impurities such as HCl, traces of sulfurous gases and possibly free chlorine.

Where free chlorine is present at this point, it may produce a serious corrosion problem in subsequent piping or equipment, and may contribute to pollution. For this reason, the reactor is carefully designed to minimize the free Cl_2 content at the reactor exit, and methane may be introduced at this point to eliminate or minimize the Cl_2 content. The reaction of methane with Cl_2 produces HCl. Also, there is a possibility of discharging substantial amounts of Cl_2, oxygen, and water during an upset in reactor operating conditions, and the use of methane to minimize oxygen and Cl_2 discharge under these conditions is helpful.

This gas is potentially valuable due to the heating content of the unburned carbon monoxide. However, practice varies as to the purification and use of the carbon monoxide values. Some chloride process operations involve scrubbing the off-gases for chlorine, HCl, and $TiCl_4$ removal and flaring or direct discharge to the atmosphere to dispose of the unwanted gas. Others follow these steps and then remove the carbon monoxide gas for use as an auxiliary fuel in the titanium tetrachloride burner.

Where flaring of the carbon monoxide-rich gas is practiced, the removal of traces of sulfurous gases, chlorine or chlorides may be required to avoid an emission problem. Scrubbing with water and an alkaline liquor in a countercurrent packed scrubber should provide satisfactory air pollution control.

The titanium tetrachloride produced in the chlorinator is purified by distillation and chemical treatment. Distillation may consist of a number of flash vaporizations, as shown in Figure 78, or it may be carried out in rectification and stripping towers. The removal of unreacted solids is accomplished by sedimentation and distillation. Generally, these operations are carried out in a pressurized system without any gaseous discharge to the atmosphere. In sections of the plant containing liquid titanium tetrachloride, particular attention must be given to the handling of relief valve vents, potential leaks, spills, sampling, etc. Titanium tetrachloride hydrolyzes spontaneously upon discharge into the atmosphere to form extremely dense white fumes of fine particle size, and even a minor leak may create emissions of high opacity.

The heart of the chloride process is the titanium tetrachloride burner. In this burner, the titanium tetrachloride is burned with air or pure oxygen, together with, in some processes, an auxiliary fuel. The auxiliary fuel may consist of carbon monoxide, from the chlorinator, or a hydrocarbon, or it may be omitted altogether. The use of auxiliary fuel permits an additional degree of freedom in controlling the temperature and chemical composition of the burner feeds.

In the specially designed burner, the oxidation of titanium tetrachloride must be completed, and crystallites of proper structure and size must be formed. In order to accomplish the chemical reaction and proper control of the crystallite structure and size, and to avoid plugging of the burner by TiO_2 deposits, the titanium tetrachloride burner design is critical. Mechanical design of the burner to produce the desired product is one of the key factors in the success of the chloride process. The reaction taking place in the burner produces free chlorine plus titanium dioxide as reaction products. The combination of the high chlorine concentration in the effluent gas, coupled with the high temperature generated in the burner (1800°C) produces a corrosive situation much more severe than that generally encountered in chemical processes. Exotic materials of construction, inorganic refractories, etc. are the rule rather than the exception in this part of the process.

The quenching of the hot combustion products in order to prevent undesirable TiO_2 sintering, the separation of the titania from the gaseous chlorine and the ultimate removal of heat from the process are among the most formidable and challenging problems encountered in a chemical process. In one process variation (NL Industries patent No. 3,560,152) the combustion products are quenched with cold recycled chlorine. The gas stream then passes to bag filters in which the TiO_2 is removed by means of Inconel fabric filter elements. Process heat removal is then accomplished by direct contact scrubbing of the hot chlorine by concentrated sulfuric acid, and the heated acid is indirectly cooled by cascade coolers. The chlorine is then recycled to the quenching step, and to the chlorination reactors. The titanium dioxide is conveyed from the bag filters, slurried in water, and further processed by wet-finishing as previously described.

Practice varies widely with regard to the method of quenching the hot burner effluent and separating the TiO_2 pigment from the hot gas. However, regardless of the approach used, there should be no interconnection of process streams with ambient air, and no potential for air pollution during normal operation.

The final pigment product is milled and packaged as in the sulfate process. These steps involve the routine recovery of pigment for product conservation, and are not significant sources of air pollution. Here again, practice in the finishing steps vary widely from one plant to another. A manufacturer may be required to process TiO_2 for a wide variety of special applications, and, therefore, need many trains of finishing equipment, including driers, reslurrying, filtering, washing and treating tanks. On the other hand, it may be possible to produce only a few products, all of which are treated in a single train.

The total amount of ventilation air required to avoid unsatisfactory working conditions in the treating area may vary from as little as 1500 SCFM to many thousands, depending on the nature and complexity of the treating equipment. However, the potential for air contaminant emissions from this part of the process is quite limited in either case.

In summary, the principal source of atmospheric emission in the chloride process is the chlorinator vent gases, consisting mainly of carbon monoxide and carbon dioxide with traces of sulfurous gases, and possibly hydrochloric acid, chlorine and titanium tetrachloride. Secondary sources are equipment and tank vent systems, but these are usually easily controlled by caustic scrubbers. Finally, special attention is required to avoid accidental spills of titanium tetrachloride, and leakage of gaseous chlorine.

3. Industry Statistics — Questionnaires —

a. Products and Raw Materials — Table 109 presents data obtained from the TiO_2 industry questionnaires on products and production. Most of the data covers the year ending 12-31-72. Total TiO_2 produced by the six plants which did not consider such data confidential was 140,040 tons by the

TABLE 109

TiO_2 INDUSTRY QUESTIONNAIRE TABULATION SUMMARY 1972*

	Production, ton/yr			Raw Materials, ton/yr						
	Sulfate		Chloride							
Plant	Rutile	Anatase	Rutile	Ilmenite	Slag	Rutile	Coke	H_2SO_4	Cl_2	Other
A	0	0	107,000	133,000		500	32,000	5,200	75,500	$19,000^3$
B	----50,000----		25,000	--	--	--				
C						Confidential				
D	0	0	45,000			50,000	16,000		6,000	
E	15,615	20,725	0		57,200			103,000		
F	0	0	25,000**	21,600***		19,300	8,000		32,000	12,000****
G	0	53,700	47,000	104,000	20,000		16,000	167,400	28,000	40,000*****
Total	140,040		249,000	258,600	77,200	69,800	72,000	275,000	141,500	---

*Plant A report period: Jan. 1 thru Dec. 31, 1970. Plant B report period: June 1, 1971 thru May 31, 1972.

**Also ships 22,500 ton/yr $TiCl_4$

***Upgraded

****Oxygen

*****Blend, 78% TiO_2

sulfate process and 249,000 tons by the chloride process. Two of the plants produced pigment by both techniques.

A summary of production and raw materials for those five plants which reported both is given in Table 110. Examination of this table reveals some interesting features. First, even though the chloride process has by far the majority of the production, ilmenite is the dominant titanium raw material with rutile maintaining a rather minor position. Second, sulfuric acid consumption in the sulfate process amounts to about 3 tons of H_2SO_4 per ton of finished TiO_2 shipped. A large part of this is potentially part of an air or water pollution problem, though a significant amount can be accounted for in the copperas by-product.

Finally, chlorine consumption in the chloride process is considerably higher than might be expected in light of the fact that chlorine recycle is employed. Making an adjustment for the $TiCl_4$ product shipped, chlorine consumption amounts to somewhat more than 1/2 ton per ton of finished TiO_2. It cannot be concluded that all of this chlorine represents potential atmospheric emissions. Instead, it may be related to the use of ilmenite ore. The manner in which ilmenite is used in the chloride process is a well kept secret. However, unless some other means are available to separate out the iron and other impurities, it is logical to assume that they are disposed of as chlorides. This could account for a large part of the chlorine consumption.

b. Process Equipment — Table 111 summarizes the major pieces of sulfate process equipment as reported in the questionnaires. The information for chloride process equipment is listed in Table 112. The degree of confidentiality required suggests that these manufacturers are somewhat hypersensitive. The data which was reported in the questionnaires reveals no startling or unusual aspects. A more detailed description of the mills in use is presented in Table 113. Only one plant reports sulfuric acid manufacturing facilities while one other has a dilute acid concentrator.

III. EMISSIONS

The emissions characteristics of the various pigment processes have been briefly discussed in the process narratives reviewed earlier. The discussion in this section will be limited to a more detailed examination of TiO_2 manufacture. This is the pigment manufacturing process whose emission potential justifies a detailed examination.

A. Description of Emission

Each of the manufacturing processes for TiO_2, sulfate and chloride, has associated with it a particular set of atmospheric pollutants. This is in addition to particulate emissions which are

TABLE 110

TiO_2 INDUSTRY QUESTIONNAIRE

PRODUCTION - RAW MATERIALS INVENTORY FROM FIVE TiO_2 PLANTS

	ton/yr
Production	
Sulfate TiO_2	90,040
Chloride TiO_2	224,000
$TiCl_4$	22,500
Raw Materials	
Ilmenite	258,600
Slag	77,200
Rutile	69,800
Leocoxene	0
Coke	72,000
H_2SO_4	275,600
Cl_2	141,500
Other Ore	59,000

TABLE 111

TiO_2 INDUSTRY QUESTIONNAIRE

SULFATE PROCESS EQUIPMENT

	Plant 1		Plant 3		Plant 5		Plant 7	
	Number	Avg. Capacity (ton/day)	Number	Avg. Capacity (ton/day)	Number	Avg. Capacity (ton/day)	Number	Avg. Capacity (ton/day)
Ore Driers	1	Confidential	1	264	CONFIDENTIAL		3	137 TiO_2
Ore Mills	3	Confidential	2	144 120			–	
Digestors	15	Confidential	6	240			8	137 TiO_2
Crystallizers	0		0				–	
Copperas Driers	0		0				–	
Calciners	4	Confidential	2	70 60			3	137 TiO_2
Pigment Mills	16	Confidential	6	78			–	

TABLE 112

TiO_2 INDUSTRY QUESTIONNAIRE

CHLORIDE PROCESS EQUIPMENT

	Plant 2		Plant 4		Plants 5 & 6		Plant 7	
	Number	Avg. Capacity (ton/day)	Number	Avg. Capacity (ton/day)	Number	Avg. Capacity (ton/day)	Number	Avg. Capacity (ton/day)
Ore Driers	1	700	0		CONFIDENTIAL		1	68.5 TiO_2
Coke Driers	0		1	20			–	
Conveying Systems	0		3	245			–	
Chlorinators	3	400	6	235			2	68.5 TiO_2
Burners	–	150	–	70			–	
TiO_2 Separation Trains	1	150	1	70			–	
$TiCl_4$ Purification Trains	1	450	1	230			–	
Pigment Mills	3	200	3	70			–	

TABLE 113

TiO_2 INDUSTRY QUESTIONNAIRE

MILLS, ETC.

Plant	Type	Number	Size
1	Ball	3	7ft x 16ft
	Roller	9	50 in. dia.
	Fluid Energy	6	42 in. dia.
	Pebble	1	6ft x 22ft
2	Micronizers	3	200 ton/day
	Sand	3	200 ton/day
	Belt Driers	2	200 ton/day
	Rotary Filters	7	200 ton/day
3	Ball	2	8ft x 6ft, 8ft x 5ft
	Hammer	6	4 ton/hr
	Micronizer	5	4-42in., 1-36in.
	Roller	1	—
4	Jet	3	36in. dia
5		CONFIDENTIAL------	
6		CONFIDENTIAL------	
7		— —	

similar for both processes.

The major sulfate process emissions can be attributed to the use of sulfuric acid. Emissions from various parts of the plant include SO_2, SO_3, H_2SO_4, sulfuric acid mist and possibly various metal sulfate particulate. The properties of these various pollutants as they pertain to emission control are sufficiently well understood, due to their widespread occurence, that discussion of their individual properties will be omitted here. Their generation in the sulfate process is such that they can all be expected to be present together in any given source. Their relative concentrations will vary from source to source and, for a given source, can vary with time and operating conditions. Furthermore, the physical properties (temperature, dew point, etc.) of the gas streams range from relatively mild to quite severe. These matters will be discussed in more detail in the next section.

Chloride process emissions include (besides ore and TiO_2 particulate) CO, HCl, Cl_2, $TiCl_4$ and coke particles. Large amounts of energy are often generated on site and this can be the source of significant amounts of emissions where oil or coal fired boilers are used.

Titanium tetrachloride hydrolyzes readily in air to produce a dense fume of finely divided particulate so that any leaks in the system or stack emission of this material tends to be very prominent. Carbon monoxide is often present in large enough quantities that its use as an auxiliary fuel is sometimes feasible.

B. Source of Emissions

1. Sulfate Process — The principal digestion reaction, in simplified form, is:

$$FeO \cdot TiO_2 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

A typical charge to the digester may consist of 1.1 to 1.5 tons of 94% H_2SO_4 per ton of ore.[36] The proportions depend partly on the composition of the ore. Water and steam are added to dilute the acid slightly and to raise the temperature. The reaction is exothermic and once initiated proceeds vigorously with considerable evolution of heat and steam. The temperature may exceed 200°C during the peak reaction period which may last from a few minutes to a half hour.

The severity of the reaction may in some cases be controlled somewhat by gradual addition of the reactants. In this way, a period of moderately high reaction will be maintained which eliminates the high peaks. Temperature in this case can be made to remain below 200°C.

The emissions from the digesters will be highly cyclical in nature. During the peak reaction periods, large amounts of steam containing SO_3, SO_2 and sulfuric acid mist will be evolved. Entrainment would be expected to be the principal mechanism by which emissions are released. The vapor pressure of H_2SO_4 for a 95% acid solution is 4.8 mm at 200°C. This is small but may still be significant. The quantity of contaminants may be reduced by using gradual addition of reactants.

Few measurements are available, at the present time, of the emissions from digester stacks. An estimate of the amount of steam evolved can be made by assuming one mole of steam per mole of sulfuric acid charged. This calculation gives about 450 pounds of steam per ton of 95% acid charged.

The calcining operation is the most critical step in the manufacturing operation as well as the most significant from a gaseous emission standpoint. Gas or oil fired rotary calciners are usually used. Temperatures as high as 900 to 1000°C are encountered at the discharge end. Residence time for the TiO_2 may be as high as 24 hours.

The hydrous titanium dioxide undergoes several washing steps prior to calcination. Even after thorough washing, however, the TiO_2 retains around 5 to 10 percent H_2SO_4.[36] This represents the most important emission from calcining. Processes have been proposed for neutralizing this residual acid with alkaline material prior to calcining, but this is not normally done.

Most of the water is removed by the time the material reaches 200°C. At this temperature, the sulfuric acid begins to evolve. Removal of sulfuric acid and SO_3 is complete at about 650°C.

The atmosphere in the calciner is reported in the literature to contain 2 to 10% oxygen on a dry basis and 30 to 50% water vapor.[36] The oxygen content of the calciner can be important in that it may influence the ratio of SO_3 to SO_2 in the exhaust gas. The reaction equilibrium between SO_3 and SO_2 may be written:

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3\ ,\ Kp = \frac{P_{SO_3}}{P_{SO_2}\ P_{O_2}}\ 1/2$$

At 650°C, the equilibrium constant, Kp, is about equal to 5 (for pressures measured in atm.) and Kp = 23 at 550°C. If the calciner is relatively rich in oxygen, virtually all the sulfur oxide should be in the form of SO_3. Where very low oxygen concentrations are present, a significant amount of SO_2 will be formed. If a slightly reducing atmosphere is maintained, even more SO_3 will dissociate. This assumes that the gas will approach equalibrium at some point in the calciner. This in turn will depend on the residence time of the gas phase and on the degree of catalytic effect in the calciner. Furthermore, the kinetics may allow an approach to equilibrium above a certain temperature but not below.

The importance of this is that it may be possible to exercise a degree of control over the SO_3 to SO_2 ratio. Economic, or other, considerations may in some cases favor the removal of one form of sulfur oxide over another.

The digestors and the calciners represent the major sources of emission in a sulfate process plant. Ore and pigment handling and grinding operations can be significant sources of dry particulate emissions. Finally, the various treatment and finishing steps are potential sources, primarily of the odor nuisance type. While the nature of such items is usually proprietary, various reduced sulfur compounds (H_2S, mercaptans, etc.) are sometimes cited as treatment agents. These have very low odor thresholds and, for those plants which use such substances, present a potential local odor problem.

2. Chloride Process — The chloride process, a more recently developed technology than the sulfate process, is subject to a greater degree of process variation from plant to plant. These variations are difficult to define since they are often considered proprietary by the practitioners of the chloride process. The chlorination and the oxidation steps are basic to the process and are always practiced in some form.

The principal source of emission from the chloride process is the chlorinator off gas. This may contain CO_2, CO, HCl, Cl_2 and small quantities of sulfur compounds (from sulfur in the coke). If air, rather than pure oxygen, is used in the $TiCl_4$ burner, then significant volumes of nitrogen will also be present in the exit gas.

The various parts of the plant which contain $TiCl_4$ are potential emission sources. Vents, relief valves and rupture disks are found in various parts of the system such as purification trains, storage tanks, etc. These can be the source, perhaps only intermittently, of the dense, white hydrolysis product formed when $TiCl_4$ comes in contact with water vapor. While the quantities from these sources tend to be small, they can present opacity problems.

As in the sulfate process, the various treatment steps offer potential problems, primarily odor. It is believed, however, that chloride process pigment requires less subsequent treatment so that the pollution potential from this source may be less than that from the sulfate process.

C. Measurement of Emissions

Each of the TiO_2 manufacturing processes deals with a different set of pollutants. The sulfate process emissions are similar to those encountered in the manufacture of sulfuric acid. The methods for measuring such emissions have been extensively developed and procedures can be found in The Federal Register (Vol. 36, No. 247, p. 24893). This method makes use of an impinger train, with a filter between the first and second impinger, and a barium perchlorate — thorin indicator titration. Some investigators have suggested that the filter should be placed before any of the impingers and the assembly heated up to and including that point to prevent the oxidation of SO_2. TiO_2 and metallic sulfate can interfere with the procedure and it is important that these be excluded from the sample. Where it is suspected that these interferents have not been totally eliminated, a sodium hydroxide — phenolphthalein indicator titration can be used to check the results, though this method will respond to any other acid substance.

The chloride process emissions include CO, Cl_2 and HCl. Carbon monoxide in chlorinator off gas is usually present in such quantities that an orsat type analysis can be performed. A procedure for measuring HCl and free chlorine is available and is described in a NAPCA document.[37] The gas sample is drawn through an impinger train using alkaline sodium arsenite in the absorbing solution. Total chlorides are determined using the Volhard titration method (back titration with ammonium thiocyanate — ferric alum indicator) on a suitably prepared sample. Free chlorine is determined by titrating an aliquot with iodine solution and a starch indicator. The Volhard chloride titration method will respond to any chloride (e.g. $TiCl_4$, $FeCl_3$) so care must be exercised in sampling the gas stream and in interpreting results.

D. Raw Data Tabulated

1. Questionnaires — A considerable amount of emission data has been reported in the questionnaires. This has been gathered together by type of operation and summarized below. Wherever possible, emissions are summarized at the process outlet before any control devices. In some cases, this has involved taking emissions at a control device outlet and back calculating using the reported efficiency for the device. It should be realized, of course, that there exists some danger in this type of approach in that a slight difference in the efficiency reported can result in a large change in the number obtained by back calculation. This is particularly true when very high efficiencies are claimed as in the present case. For this reason, the actual data reported at the control device outlet (where this is the only information given) will always be reported in the summary below as well as the calculated inlet loadings. The reader should refer to Tables 109 through 113 for production, raw material and process equipment data on these plants.

a. Digestors — Only one questionnaire (Plant 5) presented any numbers which are usable. For particulate (including sulfuric acid), emissions *after control* are 0.66 lb/ton TiO_2 produced. For SO_2, emissions are 0.31 lb/ton TiO_2. Since the details of the control device have been requested confidential, it is not possible to back calculate the emissions from the digestor stack itself. Total flow rate from the digestor stacks is reported to be 19,200 to 40,000 SCFM.

b. Sulfate Calciners — Plants 1, 5 and 7 reported emission data from sulfate process calciners. Plant 1 reports two calciners with gas flows of 65,000 ACFM and 28,000 ACFM, respectively (both at 170°F) and atmospheric emissions *after* a 95% efficient control system of 12 lb/hr and 5 lb/hr H_2SO_4, respectively. Back calculating, this translates to 30 lb H_2SO_4 per ton of TiO_2 at the calciner exit.

The same plant reports SO_2 emissions from the two calciner scrubbers as 110 lb/hr and 48 lb/hr, respectively. The scrubber system used has minimal effect on SO_2, so these can be considered to represent emissions at the calciner exits themselves. By calculation, an SO_2 emission factor of 17.1 lb/ton of TiO_2 product processed is obtained.

Plant 5 has reported SO_2 emissions from the scrubber stacks for its calciners. These calculated to be 11,830 lb/day. This results in an emission factor of 80 lb SO_2 per ton of TiO_2 produced. Insufficient information was presented to permit a calculation of an H_2SO_4 emission factor at the calciner exit.

Plant 7 reports a calciner effluent of 44,000 cfm at 950°F having a loading of 0.95 gr/cf for particulate including sulfuric acid. This resulted in a calculated emission factor of 63 lb/ton of TiO_2 for total particulate including sulfuric acid.

c. Drying and Milling — Drying and milling operations find extensive use in the TiO_2 industry whether the sulfate process or the chloride process is practiced. They can be applied to ore, coke or finished pigment. A summary of the emission information given for this area is presented in Table 114 for the sulfate process and in Table 115 for the chloride process. The last column in these tables, the emission factor, is a calculated estimate based on the information given.

The emission factors in pounds per ton of TiO_2 *product* show a good degree of consistency, with one exception, as far as orders of magnitude are concerned. This is remarkable when compared to similar data obtained for other aspects of the paint and varnish industry.

d. Chlorinators — Five plants reported some information on their chlorinator emissions, though, in general, the data was not as well defined as in the previous section. Plants reported either off gas analyses or actual emission rates for various substances. In some cases, emissions are reported after an emission control system. In other cases, either no emission control devices are present or emissions are reported upstream from such devices. In the summary that follows, an indication will be made as to whether the reported emissions are for controlled or uncontrolled processes. Finally, consistent with other sections of this report, emission factors for *uncontrolled* chlorinator emissions will be estimated.

TABLE 114

SULFATE PROCESS EMISSIONS – DRYING AND MILLING

Plant	Process	Gas Flow	Location	Loading	Control Efficiency	Calculated Emission Factor (Uncontrolled)
1	Ore drying and milling	60,000 ACFM @ 130°F	Precipitator outlet	15 lb/hr	99.8%	61 lb/ton TiO_2
3	Ore drying	5,500 ACFM @ 75°F	Filter inlet	5.2 gr/SCF	–	47 lb/ton TiO_2
3	Ore milling	3,600 ACFM @ 65°F	Filter inlet	5.0 gr/SCF	–	30 lb/ton TiO_2
5	Ore drying	12,800 ACFM @ 52°C	Filter outlet	0.02 lb/hr	99+%	*
5	Ore milling	6,300 ACFM @ 53°C	Filter inlet	0.00105 lb/SCF	–	54 lb/ton TiO_2
1	Pigment milling	38,000 SCFM	Filter outlet	6 lb/hr	99%	49 lb/ton TiO_2

*Due to the reported efficiency, no meaningful emission factor can be calculated.

TABLE 115

CHLORIDE PROCESS EMISSIONS – DRYING AND MILLING

Plant	Process	Gas Flow	Location	Loading	Control Efficiency	Calculated Emission Factor (Uncontrolled)
4	Pigment milling	368 SCFM	Mill vent	0.2 gr/SCF	–	0.67 lb/ton TiO_2
5	Ore drying	8,000 ACFM @ 88°C	Fabric inlet	0.0009 lb/SCF	–	65 lb/ton TiO_2
6	Ore drying	6,922 ACFM	Cyclone inlet	8.16 gr/SCF	–	40 lb/ton TiO_2
6	Coke drying	4,596 ACFM	Cyclone inlet	23.25 gr/SCF	–	75 lb/ton TiO_2
7	Ore drying	10,000 ACFM @ 250°F	Cyclone inlet	1 gr/CF	–	30 lb/ton TiO_2

Plants 2 and 5 present emission information from controlled chlorinator stacks. This information is summarized in Table 116. Plant 2 has given the off gas analysis for various years. Of interest are the trends of improvement for all reported constituents except carbon monoxide. Plant 5 has reported actual emission rates.

Plants 4, 6 and 7 have reported data for either *uncontrolled* chlorinator stacks or for conditions *upstream* from control equipment. Plant 4 reports a typical off gas analysis which is tabulated in Table 117. Emissions of $TiCl_4$ for this plant were reported to be 22 to 88 lb/hr.

Plant 6 has listed emissions directly out of the chlorinator tail gas stack. These are also summarized in Table 117. Emission factors for chlorine and HCl are 4.3 lb/ton TiO_2 and 39 lb/ton TiO_2 respectively. This plant has presented a complete emission inventory of 48 sources which includes boilers, chlorinator, dryers, kilns, tank vents, etc. Table 118 lists emissions for the power house, chlorinator, and the total for all sources including power house and chlorinator. Examination of the table indicates that the power house and chlorinator account for the major fraction of total emissions from this chloride process plant.

Finally, plant 7 has listed uncontrolled emissions from its chlorinator off gas as including 1 lb-mole $TiCl_4$/hr and 6 lb-moles HCl/hr. Correlating these with production, emissions factors for $TiCl_4$ and HCl are obtained which calculate to be 67 lb/ton TiO_2 and 77 lb/ton TiO_2 respectively.

Plants 2 and 5 present emission information from controlled chlorinator stacks. This information is summarized in Table 116. Plant 2 has given the off-gas analysis for various years. Of interest are the trends of improvement for all reported constituents except carbon monoxide. Plant 5 has reported actual emission rates.

Plants 4, 6, and 7 have reported data for either *uncontrolled* chlorinator stacks or for conditions *upstream* from control equipment. Plant 4 reports a typical off-gas analysis which is tabulated in Table 117. Emissions of $TiCl_4$ for this plant were reported to be 22 to 88 lb/hr.

Plant 6 has listed emissions directly out of the chlorinator tail gas stack. These are also summarized in Table 117. Emission factors for chlorine and HCl are 4.3 lb/ton TiO_2 and 39 lb/ton TiO_2, respectively. This plant has presented a complete emission inventory of 48 sources which includes boilers, chlorinator, driers, kilns, tank vents, etc. Table 118 lists emissions for the power house, chlorinator and the total for all sources including power house and chlorinator. Examination of the table indicates that the power house and chlorinator account for the major fraction of total emissions from this chloride process plant.

TABLE 116

CHLORINATOR EMISSIONS AFTER CONTROL

Plant 2 - CHLORINATOR OFF GAS
TYPICAL ANALYSIS — PERCENT

Constituent	1972	1971	1970	1968 to 69
Cl_2	0.00006	0.0001	0.0001	0.0001
SO_2	0.00007	0.0012	—	—
Cl	0.056	1.5	2.0	3.0
O_2	2.7	4.0	4.0	4.0
CO_2	25.5	30.0	30.0	22
CO	27.5	24.0	24.0	26.0
N_2	44.0	40.0	40.0	45
TiO_2	3 lb/hr	6 lb/hr	8 lb/hr	12 lb/hr

Plant 5 - CHLORINATOR OFF GAS
EMISSIONS — LB/HR

Constituent	Rate, lb/hr
NO_x	0.34
CO	1570
Particulate	0.82
Cl_2	10

TABLE 117

CHLORINATOR EMISSIONS BEFORE CONTROL

Plant 4 - CHLORINATOR OFF GAS TYPICAL ANALYSIS, PERCENT

Constituent	%
N_2	5 to 10
CO_2	50 to 70
O_2	0.5 to 2.5
CO	10 to 20
$TiCl_4$	0.2 to 0.5
HCl	0.1 to 0.5
$SiCl_4$	0.1 to 0.4

Plant 6 - CHLORINATOR EMISSIONS, LB/HR

Constituent	Emission Rate
SO_2	0.00
Particulate	0.00
NO_x	1.05
CO	3,195.00
Hydrocarbons	0.00
Cl_2	53.00
HCl	420.00

TABLE 118

Plant 6 - EMISSION INVENTORY

Constituent	Power House lb/hr	Chlorinator lb/hr	Total All Sources lb/hr
SO_2	855.0	0.00	855.13
Particulate	104.0	0.00	126.38
NO_x	130.2	1.05	140.57
CO	17.4	3,195.00	3,213.94
Hydrocarbons	8.4	0.00	10.84
Cl_2	—	53.0	86.40
HCl	—	420.0	422.2

Finally, plant 7 has listed uncontrolled emissions from its chlorinator off gas as including 1 lb-mole $TiCl_4$/hr and 6 lb-moles HCl/hr. Correlating these with production, emissions factors for $TiCl_4$ and HCl are obtained which calculate to be 67 lb/ton TiO_2 and 77 lb/ton TiO_2, respectively.

e. Summary of Emission Factors — The above information was used to calculate the emission factors presented in Table 119 for the various steps in TiO_2 pigment manufacture. It should be emphasized that these represent estimates for *uncontrolled* processes. Most of the plants reported emission control equipment on most of these processes. Where required, stated control efficiencies and outlet loadings were used to back calculate the uncontrolled emission factor. With the exception of SO_2 and CO, existing controlled plants report a significant reduction in emissions from the levels suggested by the emission factors. Sulfur dioxide and carbon monoxide are relatively unaffected by the types of control devices presently in use.

It should be emphasized here that considerable variation exists in the manner in which these various process are run, particularly the chlorinators. The emissions from chlorinators can be a function not only of control devices but also of process variations, type of ore used, etc. Since much of the technology in this area is proprietary in nature, not all processing options are available to all producers. Consequently, a producer operating a process that is *inherently* higher in emissions than a process used by some of his competitors may not be able to achieve as low emissions by process modification and may require the addition of an economically unfeasible amount of control equipment. This could put him in a non-competitive position if uniform emission standards were set for the industry.

One other source of emission is mentioned in one of the questionnaires which seems to be unique to that particular plant (Plant 4). This plant reports a significant emission of sulfur monochloride, S_2Cl_2, from an off gas stream from the $TiCl_4$ oxidizer. Emission rates of 5.1 to 22 lb/ton of TiO_2 produced are reported. In the normal operation of the chloride process, the oxidizer does not vent to the atmosphere directly so that the precise source of this emission is not clear. It is believed that, as this plant operates the chloride process, S_2Cl_2 is used to temporarily absorb the chlorine from the oxidizer. Chlorine recycle can then be accomplished by stripping the absorbed material from the S_2Cl_2. The S_2Cl_2 emissions may result from the tail gas from a chlorine absorption step.

2. Other Sources — Two other sources of information have been obtained on digestor emissions. The St. Louis County Health Department supplied test results for the NL Industries sulfate plant in St. Louis. They report emissions downstream from a set of scrubbers to be "nil" for sulfuric

TABLE 119

ESTIMATE OF EMISSION FACTORS FOR UNCONTROLLED PROCESSES

Process	Pollutant	Emission Factor* (lb/ton TiO_2 Produced)
Sulfate Digester**	H_2SO_4	14.1
	SO_3	8.8
	SO_2	4.2
	H_2S	0.9
Sulfate Calciner	H_2SO_4	46
	SO_4	48
Ore Drying		
Sulfate	Particulate	47
Chloride	Particulate	44
Coke Drying	Particulate	75
Ore Milling		
Sulfate	Particulate	42
Chloride	Particulate	—
Pigment Milling		
Sulfate	Particulate	49
Chloride	Particulate	—
Chlorinator	$TiCl_4$	32
	Cl_2	4.3
	HCl	55
	CO	260

*These are average emission factors. Ranges are given on the preceding tables and discussed in the text.

**Emission factors for this process based on paper by L.L. Falk discussed in the following section. The remainder of the factors based on the TiO_2 Industry Questionnaires.

acid and 7 lb/hr for SO_2. These scrubbers are claimed to be "100%" efficient for H_2SO_4 so it is not possible to determine the inlet loading.

The best defined information obtained thus far is contained in a paper presented by L. L. Falk.[38] He reports digestor emissions from the duPont plant in Baltimore (not included in the questionnaires). Figure 79 gives total gas evolution from the digestor as a function of time after oleum addition. It can be seen that the reaction proceeds at a negligible rate for about the first 45 minutes and then proceeds at a vigorous rate for a very short period of time. A considerable amount of gas (mostly steam) is evolved during this period.

Typical emissions per batch are given below:

Material	lb/batch
Steam	8,000
H_2SO_4	120
SO_2	36
H_2S	8
SO_3	76

The quantity of materials charged to the digestor in a typical run was not given but it is possible to make an estimate. Assume a batch charge of 20 tons of ilmenite (Barksdale, p. 220). Further assuming the ilmenite to contain 50% TiO_2, and overall plant recovery to be 85%, the emission factors can be estimated as follows:

Emission Factors for Sulfate Process Digestors

Emission	Quantity (lb per ton TiO_2 Product)
Steam	940
H_2SO_4	14.1
SO_2	4.2
H_2S	0.9
SO_3	8.8

Atmospheric emissions tests on the National Lead Company, Sayreville, New Jersey, sulfate process plant was conducted by the Division of Air Pollution of the Public Health Service in September, 1966.[39] This plant has seven calciners. The sampling team tested the emission control system for one of the calciners. The system consisted of an initial water scrubber, followed by electrostatic precipitators, followed by another scrubber. A sketch of the system is shown in Figure

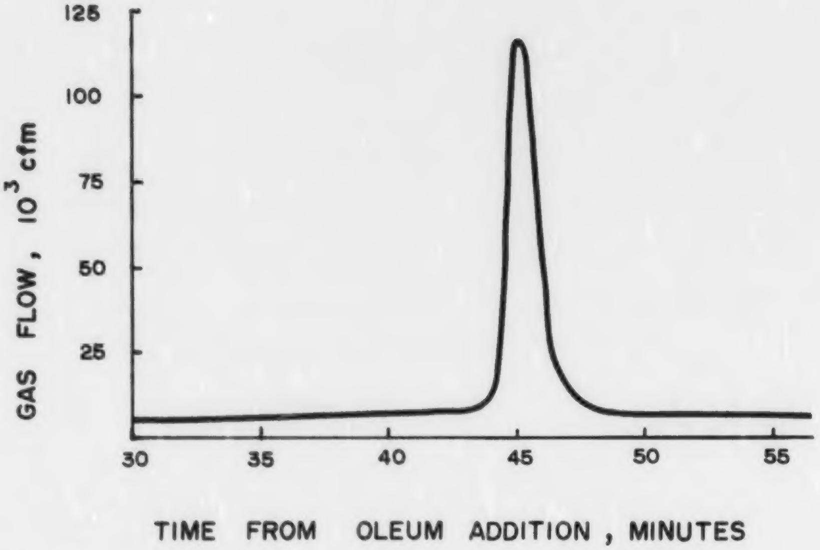


FIGURE 79

EXHAUST RATE FROM SULFATE PROCESS DIGESTION TANKS

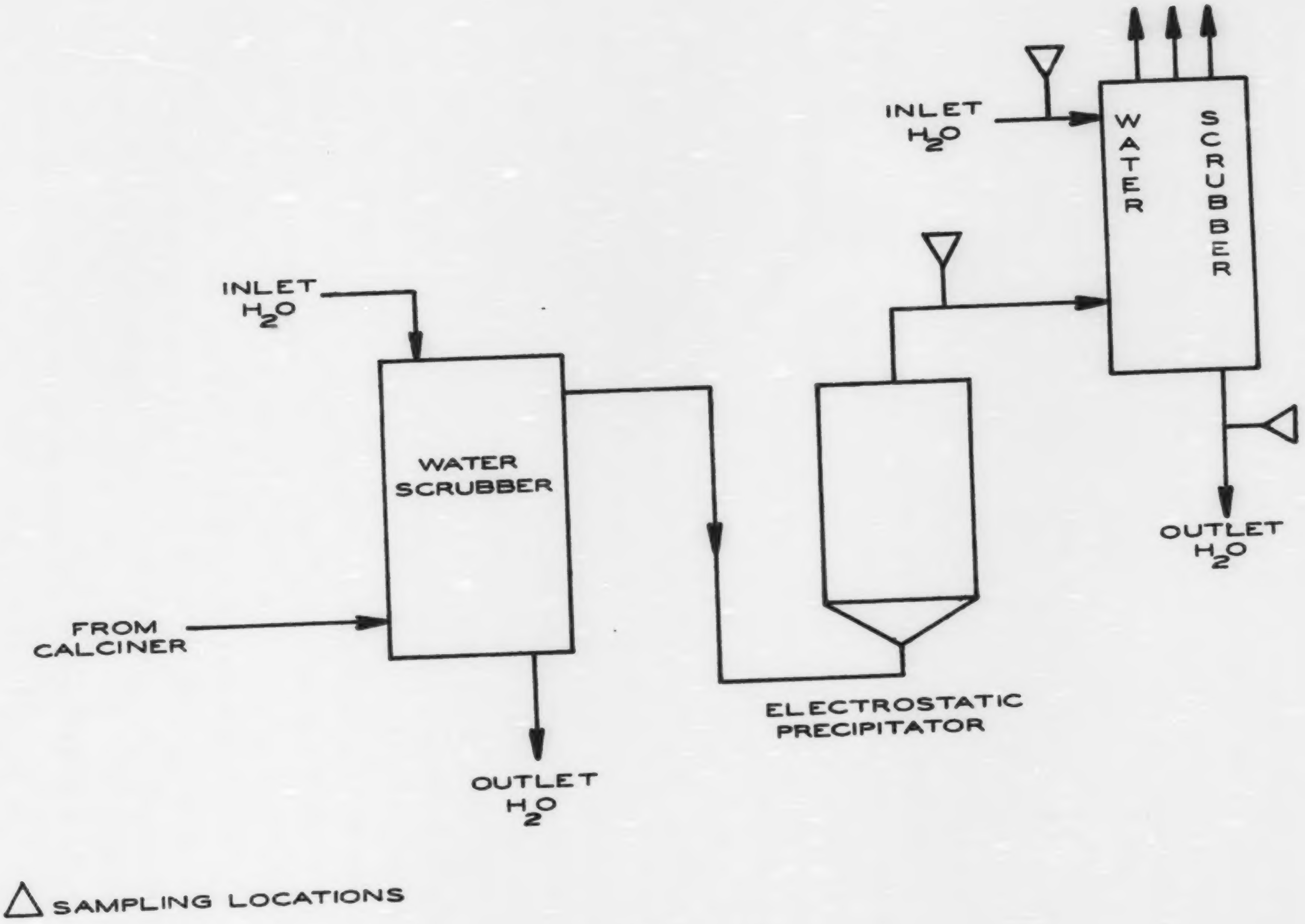


FIGURE 80

CALCINER EMISSION CONTROL SYSTEM

80. They were unable to obtain reliable measurements at the calciner outlet (due to interference with the analytical technique from TiO_2) and made no attempt to monitor the exhaust from the first scrubber. They reported the results of measurements at the outlet from the precipitators and on the water from the last scrubber. The average results obtained after the precipitators are shown in the following table:

Pollutant	Rate (lb/day)
SO_2	7,900
SO_3	310
Particulate	380
Acid Mist	180

Total gas flow rate at this point was measured (on a dry basis) to be about 3×10^7 SCF/day. Several comments should be made before making any conclusions from this data. First, the results of individual runs showed deviations of as much as a factor of two. It is not known whether these are due to inherent difficulties in obtaining good samples or whether there are, in fact, large fluctuations in the calciner exhaust.

The quantity of emissions reported raises some questions. It was assumed by the sampling team that each calciner handles about the same amount of material. If this is correct, then the calciner in question processes about 62 ton/day of TiO_2. If the charge had retained 10% H_2SO_4, then this would result in an emission of about 4 tons of sulfur (as SO_2) per day. It can be seen that the SO_2 reported after the precipitators is about sufficient to account for almost the entire total. It is not known how much SO_2 had been removed by the first scrubber nor how much acid mist was removed in the precipitators.

If these devices account for considerable amounts of sulfur oxides, then the reported emissions seem to be too high. On the other hand, most of the calciner exhaust emissions can be in the form of SO_2 only if a somewhat reducing atmosphere is maintained in the calciner. Since no information is available on these aspects of the problem, some caution should be exercised in accepting the data as typical.

NL Industries has reported that, due to an error in the method of calculation, the Public Health Service results are high by a factor of two. Variable oxidation of sulfite to sulfate in the last tower was felt to have further increased the error, making the results high by perhaps as much as a factor of three.

In view of the above comments, several suggestions can be made for source testing. If at all possible, the calciner exit itself should be sampled. The problem here is that TiO_2 particulate may interfere with the analysis for sulfate. Techniques should be sought to overcome this.

It should be determined whether the calciner operates in a relatively steady state condition or whether large fluctuations occur in operating conditions. A sample of the TiO_2 cake prior to calcination should be obtained and analyzed for sulfuric acid. This, plus a knowledge of the calciner throughput, should provide a good estimate of the total emissions. Finally, an analysis of the calciner exhaust for oxygen would provide a means to check whether the SO_3 to SO_2 ratio measured is reasonable.

IV. EMISSION CONTROL TECHNOLOGY

A. Description of Currently Used Control Systems

Table 120 summarizes the particulate emission control devices reported in the questionnaires. Included in this table are those devices which collect dry, solid particulate from drying and milling type operations only. Table 121 discusses those devices whose purpose is to control processes applicable only to TiO_2 manufacture such as digestion, chlorination, etc. Plant 4 reported no emission control at all, while plants 5 and 6 considered at least part of the information proprietary.

A wide variety of devices is reported including cyclones, fabric filters, several varieties of scrubbers and electrostatic precipitators. There are several instances of devices connected in series in order to obtain good control. Over all control efficiencies, where reported, are said to range from 90 to 99+% depending to some extent on the process being controlled.

B. Other Methods of Control

Most conventional pollution control devices that would be applicable to the types of emissions found in TiO_2 plants are presently in use. The application of more advanced concepts is discussed in Chapter 9.

C. Performance of Currently Used Control Systems

Performance data on presently used systems, as reported in the industry questionnaires, is included in Tables 120 and 121 listed earlier. For particulate control devices, efficiencies up to 99%, and higher, are reported. Such efficiencies, on a weight basis at least, can be achieved under favorable conditions with the types of devices in use. Beyond that, it is not possible to comment on the accuracy of the reported performance figures. It is not known whether the efficiencies are based on actual tests.

For other processes (calciners, chlorinators, etc.), data on efficiencies is not consistently

TABLE 120

TiO$_2$ INDUSTRY QUESTIONNAIRES

PARTICULATE CONTROL DEVICES

Plant	Process	Type of System — Number of Devices	Flow (cfm)	Inlet Loading (gr/SCFM)	Efficiency	Ratio Air/Cloth
1	Ore drying-milling	Elec. precipitator	–	–	99.8	
	Pigment mill	Fabric filter — 11			99	2.0
2	Driers	Cyclone	1,000	–	–	–
	Pigment transfer	Fabric filter — 2	1,250	–	–	–
	Dry mills	Wet scrubber-venturi scrubber — 2	500	–	–	–
3	Ore driers	Fabric filter	5,500	5.2	99+	2.8
	Ore mills	Fabric filter	2,160	5.0	99+	3.2
	Ore mills	Fabric filter	1,440	5.0	99+	3.2
	Pigment mills	Venturi scrubber	450	–	–	–
	Pigment mills	Wetted baffle — 4	1,000 to 1,800	2	90	–
	Pigment mills	Fabric filter	1,000	–	99 (est.)	0.24
4	None					
5	Ore driers	Fabric filter	12,800	–	99+	4.8
	Ore driers	Fabric filter	8,600	6.3	99+	3.2
	Ore mills	Fabric filter	6,300	7.4	99+	3.1
	Pigment mills	CONFIDENTIAL				
6	Ore driers	Cyclone	6,922	8.16	94+	
	Coke drier	Cyclone-spray w/hydrofilter	4,596	23.25	99	
	Power house	Multi-cyclones — 2	55,[illegible]00	–	89	
	Spray drier	Cyclones — 4	49,020	7.32	99	
		Venturi scrubber				
7	Ore drier	Fabric filter	2,500	0.5	95	5
	Chloride ore drier	Cyclone	10,000	1	99	
	Chlorinator waste pit	Venturi scrubber	1,600	18.2	92	

TABLE 121

TiO_2 INDUSTRY QUESTIONNAIRES

EMISSION CONTROL DEVICES

Plant	Process	Type of System — Number of Devices	Flow (cfm)	Pressure Drop in. w.c.	Efficiency %
1	Digestion tanks	Wetted wall scrubbers — 5	–	–	–
	Calciners	Spray tower → venturi — 2	–	40	95%
2	Chlorinator $TiCl_4$ purification	[Water scrubber Lime scrubber]	12,000	–	–
	Waste chloride vent	Venturi scrubber	2,000	–	–
	Oxidizer and pigment Separation, "snake" system for local collection	8% lime baffle plate Scrubber	9,000	–	–
	"Emergency scrubber" for oxidizer & TiO_2 separation equipment	Packed column 15% NaOH	4,700	–	–
3	Digestion tanks	Multi-spray — 3	2,000 to 3,300	1/2	–
	Calciners	[2 stage spray chamber — 3 Elec. precipitator — 3 Multi-spray — 3]**	24,000	2	99%
4	None				
5	Digestion tank	----------------CONFIDENTIAL------------			
	Calciners	----------------CONFIDENTIAL------------			
	Chlorinator	----------------CONFIDENTIAL------------			
6		----------------CONFIDENTIAL------------			
7	Digestors	Scrubber	25,000	5 in.	
	Calciners	Cyclone → scrubber → elec. precip.	44,000 ACFM	2 in. → 3 in. → ?	32% → 81% → 64%
	Chlorinator	Spray → venturi → impingement	3,230	45 in.	[90% $TiCl_4$ 99% HCl]
	$TiCl_4$ Purification/storage	(same as above)			

*Control devices in series

**3 parallel systems with control devices in series reported. For calciners, three plants report efficiencies in excess of 90%. The basis of calculation is not stated. In each case, the emission control system consists of two or more devices in series.

One plant reported control efficiency for a chlorinator emission control system. Efficiency of 90% or better was reported for $TiCl_4$ and HCl. An overall pressure drop of 45 inches of water through three devices in series (one a venturi scrubber) suggests that the level reported is not unreasonable. As before, however, no further evaluation of the data can be made.

CHAPTER 9

RECOMMENDED RESEARCH AND DEVELOPMENT PROGRAMS

Significant among the purposes of this industry study is the recommendation of Research and Development programs which can lead to improvement in air pollution measurement and control. In the following pages, the deficiencies in both air pollution technology and emission measurement are treated in detail. Consideration is also given to that control technology which is more efficient than "best control" but is considered to be economically unfeasible. Based on the findings of the Research and Development study presented herein, priorities to improve control technology are recommended along with suitable programs to achieve these improvements.

I. EMISSION CONTROL TECHNOLOGY

The areas of control technology within the coating industry which would benefit most by the application of research and development efforts are described. In those segments of industry where a problem has been selected, an attempt has been made to assess the probable requirements in time and cost for successful program accomplishment.

A. Technical Developments for Reduced Levels of Emission

The areas where improvements could be made to reduce levels of emission are categorized as follows:

PROCESS CHEMISTRY AND KINETICS
PROCESS EQUIPMENT AND/OR OPERATIONS
CONTROL EQUIPMENT AND/OR OPERATIONS

Requirements in these categories are outlined below.

1. Process Chemistry and Kinetics — Odor and solvent emissions from opened and closed kettles represents one of the major air pollution problems for the industry, due primarily to the local nuisance problem generated by this type of emission. Cooking in open kettle has dropped off to the point where it no longer deserves further attention. Most resin and varnishes are now cooked in closed kettles which have resulted in significant reduction in emission levels. These emissions could be further reduced if process chemistry or cooking formulas could be developed for processing in a truly closed or pressurized kettle.

2. Process Equipment and/or Operations — Raw material handling as well as process chemistry also must be developed for the use of pressurized kettle cooking. These are required to allow for addition and removal of materials during the cook while still maintaining a closed system. Development of an in-line, closed thinning, blending and filtering system for handling of the materials after cooking would also substantially eliminate the emission currently encountered with existing thin tanks and leaf filters.

3. Control Equipment and/or Operations — Although a wide variety of air pollution control devices are used in the paint industry, only a few types may be considered applicable. These are:

Thermal and catalytic afterburners for cooking operations

Scrubbers or condenser-scrubbers for cooking operations

Fabric collectors for milling, grinding and other dry solid processing operations

The principal deficiencies associated with the operation of afterburners fall into two categories:

1. Those problems dealing with the inherently large fuel consumption and cost.
2. Potential for safety hazards and damage to the equipment by fire or explosion.

The first of these two problems is becoming increasingly urgent as natural gas becomes more difficult to obtain. The second problem has caused numerous casualty losses, as well as injury to employees over many years in the cooking industry.

For those process reactions which are not amenable to closed or pressurized cooks, or in circumstances where physical or capital limitations do not permit replacement of the present cooking equipment, a more economical form of oxidation, with regard to operating cost and fuel conservation, is needed. Three directions suggest themselves for the correction of deficiencies in afterburner systems for kettle operations. These are:

1. Improved heat exchanger efficiency for thermal afterburner units
2. Improved activity and stability of catalysts for use in catalytic afterburner units
3. Direct flame incinerator

Of these three, a direct flame incineration system of low first cost offers the most potential to provide optimum cost-benefit relationships for the public.

Thermal afterburners are inherently expensive. Their capital cost increases as the gas flow rate increases, almost without relationship to the concentration of organics in the fume stream. The addition of heat exchangers increases thermal efficiency, decreases operating cost and significantly increases initial capital cost. The best heat exchangers of conventional design (i.e. fixed tube exchangers and rotary matrix heat exchangers) have thermal efficiencies on the order of 60 to 70%. Some nonconventional regenerative designs using fixed beds of checkerwork, stone, etc. are being offered with design efficiencies in the range of 80%. Continued competition among the manufacturers of afterburner equipment is likely to lead to marginal improvements in the relationship between first cost and heat exchanger efficiency. Therefore, it is not felt that thermal oxidation should be considered as an area for funded R&D work.

Catalytic afterburners have been used for many years in the abatement of organic fumes from kettle cooking operations. Operations on a single kettle tend to be widely varied as alternative formulations are prepared, and, therefore, the potential for inclusion in the cook of one or more catalyst deactivating or poisoning agents is always present. The problem of maintaining activity in the presence of contaminating or deactivating agents becomes increasingly severe as the improved catalyst performance is desired. For example, a catalyst requiring 1,000°F inlet temperature to oxidize toluene is only marginally better than a thermal system with no catalyst at all. This low level of activity is likely to be quite tolerant of poisons, misoperation and the like. On the other hand, a very active catalyst, capable of oxidizing toluene at 450°F is likely to exhibit a marked sensitivity to overheating, contamination, etc. The "fine edge" of activity is easily damaged by a variety of chemicals and by non-uniform or extreme operating conditions. These factors suggest that a major R&D effort should not be made in the area of catalyst development.

Since most emission from kettle cooking is high enough in combustible concentration to be flammable, the direct flame incinerator discussed earlier in Chapter 5 offers great potential for incineration with little or no fuel cost. These units are also commercially available. The area of research and development required is in the transfer system from the kettle to the unit.

B. Economic Deficiencies Preventing Reduced Levels of Emissions

The minimum size of the independent paint manufacturer is quite small. Even seemingly modest demands for pollution abatement equipment may present a substantial economic burden to a small independent. Probably the most difficult problem for the small manufacturer is the prevention of solvent loss during transfer, storage and mixing processes. Of these, those losses associated with storage of solvents are most likely to be of concern to air pollution agencies, and most difficult for the small manufacturer to cope with. The small scale of these emission problems and the high cost-benefit relationship for emission control systems present a difficult economic problem.

C. R&D Priorities to Improve Control Technology

Four R&D programs have been selected as a part of this industry study to improve control technology. These programs are as follows:

1. Closed Reactor Design Program
2. Investigation of Methods for Handling Resin Raw Materials in the Liquid Form
3. Development of Inexpensive Scavenging Systems
4. Development of Transfer System for Direct Flame Incineration

The details of these programs along with the work and cost requirements are detailed in the next report section.

D. Recommended Programs for Achieving R&D Requirements

1. Closed Reactor Design Program — This program involves the analysis of requirements for general purpose reactors to produce resin and varnish products in a completely closed reactor system.

The following paragraphs list the program steps envisioned in the overall R&D program:

1. Detailed library investigation of equipment literature and patent literature pertaining to closed reactor systems already developed.
2. Detailed investigation of the nature and scope of individual reactions carried out in existing kettles.
3. Reduction of the physical and chemical requirements of the cooking process to simple concepts regarding those factors which determine the nature of the equipment required.
4. The specification of a design basis for a non-ventilated reactor system.
5. The collection of potentially feasible designs for review and screening.
6. The selection of alternative equipment types which appear generally suitable for the requirements in the prototype specification.
7. The fabrication and testing of a prototype reactor.

The proposed program would be conducted in three phases consisting of:

1. Research and selection of approach
2. Design and construction of prototype
3. Field testing of prototype

Phase I should involve approximately 1,000 man-hours of professional R&D work, and about 600 man-hours of non-professional effort. The total estimated cost for this phase is $35,000. *Phase II* should consist of a design portion requiring approximately 750 man-hours of professional and non-professional time. The total estimated cost of the labor is approximately $28,000. In addition, a one-time fabrication cost of the prototype reactor is estimated at $40,000. The total for *Phase II* is estimated at $68,000.

Phase III, the installation and field operation of the prototype, will vary in cost depending upon the ability to arrange with a commercial paint manufacturing company to contribute to the installation and operating costs for the kettle required. The estimated cost of this phase of this program is in the range of $100,000 to $150,000 depending on final commercial arrangements. Of this total, $25,000 is included to cover an estimated 900 man-hours of field test and observation work.

2. Investigation of Methods for Handling Liquid Resin Compounds — This investigation involves an analysis of methods for handling resin components in liquid or molten form. The inherent problems with solid resin powders are two-fold:

1. The ventilating air requirement is large in order to prevent fuming through the kettle hatch.
2. The added powders tend to become airborne and are swept out of the hood.

Solid raw materials can potentially be handled in liquid or molten form so that batch additions could be made without handling dry powders. The handling of molten salts at elevated temperatures is feasible and has been demonstrated in other industries and should not involve any radically new techniques. The potential problems lie in the development of equipment which can be operated economically and safely, particularly in connection with small, unsophisticated cooking operations. The R&D program consists of three phases which are outlined below:

Phase I consists of a literature search to accomplish the following:

1. Review existing technology and define the types and extent of usage of solid raw materials in resin cooking.
2. Establish the properties of the identified components, including: fusion point, viscosity, vapor pressure, corrosiveness, stability and other properties.

In addition, literature research and a field investigation should be made on conventional equipment for handling molten materials in other manufacturing activities.

Phase II should include a definition of alternative process schemes and equipment components. Based on this definition, an economic evaluation of alternative process schemes and equipment should be made.

Phase III should consist of the selection and definition of a prototype process scheme for handling molten salts in the paint and varnish industry.

In this program, field testing of the proposed prototype system is not considered an essential step. The development of a system design which is reasonable from an engineering standpoint combined with publication of the bases, calculating methods, etc., used should be sufficient to make proposed system available to designers of new plants in the coating industry.

The cost and timing for the three phases of the proposed program are as follows:

Phase I should require approximately 320 man-hours of engineering and scientist work and cost about $10,000.

Phase II will require about 320 man-hours of engineering work as well as 160 man-hours of drafting and should cost approximately $13,000.

Phase III consists of about 320 man-hours of engineering work and 160 man-hours of drafting and should cost approximately $13,000.

3. Development of Inexpensive Solvent Scavenging Systems — This development program is proposed with particular emphasis on the needs of the smaller paint manufacturers. The proposed program considers the development of a simple and inexpensive system for scavenging solvent vapors from storage tanks and possibly from transfer points as well.

Three basic mechanisms deserve consideration in limiting solvent emissions: prevention of evaporation, incineration of the tank effluent and adsorption of organics from the vented gases.

The steps in this proposed program are as follows:

1. Literature and plant surveys to establish the size and type of solvent storage tanks most widely used in the industry.
2. Library and plant surveys to establish the most frequently used solvents as well as the physical properties of these solvents.
3. Preparation of calculated emissions, and comparison of these with test results prepared by the EPA.
4. Formulation of performance criteria for abatement systems.
5. Screening of available mechanisms for abatement, and selection of the most feasible approach to handle each of the following:
    a. Prevention of Vaporization
    b. Condensation
    c. Thermal Incineration
    d. Activated Carbon Adsorption

6. Preliminary design of a system utilizing each mechanism.
7. Analysis of the alternative designs for selection of the most economical design approach.
8. Preparation of a prototype design.
9. Construction and testing of the prototype design.

This program can be conducted on a relatively modest scale. The research and design phases should not entail more than 700 hours of professional work and 400 hours of drafting. The cost for this part of the work is estimated at $20,000. Fabrication of the prototype and subsequent testing is estimated at an additional $30,000.

4. Development of Transfer System for Direct Flame Incineration — Direct flame incineration would offer a very inexpensive system to build and operate. It would also reduce the danger of fires and explosions currently being experienced by this industry. The main problems preventing use of this system are:

1. Excessive ventilation of reactor kettles when loading materials. This system will work better with the closed pressurized reactor discussed earlier.
2. The need for a gas tight low flow process blower capable of pumping the reactor effluent which will contain resinous material and phthalic anhydride particulate. Corrosion and heat resistance must also be considered.
3. The need for automatic safety valves to meet the requirements outlined in Item 2.
4. The need for a nozzle mix burner to meet the requirements outlined in Item 2.

The program proposed would be carried out in three phases and would follow the same approach outlined for the *closed reactor design program*. The three phases would consist of:

1. Research and selection of approach
2. Design and construction of prototype
3. Field testing of prototype

Costs and man-hour requirements are estimated to be about 65% of those presented for the *closed reactor design program*.

II. MEASUREMENT OF EMISSIONS

Significant attention has been devoted to the development of techniques and instruments for testing particulate and organic emission in general. In the paint and varnish industry, certain deficiencies in measurement exist due to the nature of the cooking process which suggest the need for additional development work. These deficiencies and required development work are outlined below.

A. Deficiencies in Manual Methods of Source Sample Collection and Analysis

The cooking process is a cyclical batch operation with respect to gas flow and hydrocarbon concentration. In order to produce an accurate assessment of the total emissions per batch (or average emission), it is essential to undertake simultaneous measurements of both gas flow and of organic concentration over a period of several hours. Using manual source testing methods, this is both an imperfect and cumbersome procedure at best.

The resinous materials vaporized from the cook have high dew-points, and, therefore, readily condense on any surface which is at a temperature lower than that of the air contacting the resinous mass. This leads to deposition of organic material in any sort of sampling system which operates below the temperatures involved in the cooking operations (as high as 700°F). These deposits are troublesome for mechanical reasons and also since they cause emissions into the gas stream at periods substantially later than the time they enter the sampling system.

B. Deficiencies in Techniques and/or Equipment for Continuous Monitoring of Source Emissions

Continuous monitoring of cooking operations is subject to the same deficiencies as described previously for manual testing methods. In the case of condensation of resinous materials, the continuous methods are significantly more sensitive than the manual methods. This is primarily due to the necessity for somewhat remote location on continuous monitoring equipment and the attendent long length of sample lines.

Such continuous equipment, as is presently available, is very sensitive and is designed more for laboratory use than for the production plant. Long sample lines are usually required as well as a host of auxiliary materials such as calibration gases, etc. A further deficiency exists in that present continuous monitoring equipment is incapable of continuous operation over long periods without regular attention by highly skilled instrument specialists.

C. R&D Priorities to Improve Measurement Techniques

Based on the deficiencies which exist in measurement of emissions in the paint and varnish industry, only one R&D program is suggested. This program is to develop a simple and inexpensive instrument to detect hydrocarbon emission and measure flow from kettle cooking operations. The proposed program is outlined in the next report section.

D. Recommended Programs for Achieving R&D Requirements

An ideal monitoring instrument for kettle cooking operations would simultaneously measure the gas flow and the concentration of total organic materials in the gas stream. In this manner, a weight rate of emission of organics could be deduced, or even generated within the instrument and recorded. This instrument would be required to run continuously over long periods of time without the necessity for highly skilled instrument specialists. It would either operate with the detection element deployed directly in the gas stream and without inter-connecting sampling tube, etc., or with the entire sampling train operated at a temperature high enough to prevent condensation of organics. It is, of course, imperative that the instrument pose no safety hazard.

The characteristics of this instrument are as follows:

1. Organic concentration and gas flow rate must be measured simultaneously.
2. Organic concentration must be measured in terms of either total hydrocarbon or equivalent methane.
3. Continuous operation must be possible on heavy organic fumes from kettle operations.
4. Maintenance or operation requirements must be simple.
5. First cost must be inexpensive (less than $5,000).

In addition to handling organic emissions, the proposed instrument would need to incorporate total flow measurement capability with low energy loss or pressure drop. Primary flow elements and associated connection lines will need to be designed to operate at high temperature and without interference from deposits of heavy resinous materials.

With a low pressure drop limitation, the selection of the primary flow measurement device should be limited to the following:

1. Pitot tube (S type)
2. Venturi flowmeter
3. Fluidic sensor

The final selection of device and means for eliminating interference from organic deposition would be a part of the proposed development program. In addition, the program would include selection of a read-out approach which would be most compatible, least expensive and require the lowest maintenance.

The proposed development would be carried in three phases as follows:

1. Library and field research.
2. "Bread board" and flow measurement experimentation.
3. Design and fabrication of a working prototype.

The suggested content of each phase is as follows:

Phase I

1. Literature survey to define the present state of the art for flame ionization detection as well as pitot or venturi flow measurement.
2. Discussions with vendors to establish the range of commercially available pitot and venturi measuring devices.
3. Definition of alternatives with respect to:
   a. Detector configuration
   b. Electronic circuitry
   c. Hydrogen generation
   d. Over-all packaging
   e. Primary flow measurement
   f. Sample-loop consideration

Phase II

1. Assembly of test set-up.
2. Preparation of alternative "bread board" detectors.
3. Selection of primary flow devices.
4. Testing modification of bread board units and alternative flow devices.
5. Selection of mechanisms applicable to prototype design.

Phase III

1. Prototype design
2. Component acquisition
3. Fabrication of components
4. Assembly of components
5. Field trials
6. Revision of prototype as required
7. Final testing

The timing and costs for each of the three phases are indicated below:

Phase I should require approximately 400 man-hours of engineering or scientist effort and cost approximately $10,000.

Phase II is expected to require 1500 man-hours of engineer or scientist effort and 1000 man-hours of technician effort. This phase of the program should cost approximately $45,000. In addition, equipment costs of $5,000 would be anticipated.

Phase III should require approximately 1500 man-hours of engineer or scientist effort and 2000 man-hours of drafting and technician effort which will cost about $65,000. In addition, about $8,000 will be required to purchase components. It is anticipated that installation and operation of the prototype unit can be arranged with a paint manufacturer and that it will be an advantage for him to bear the installation and operation expense.

III. PIGMENT INDUSTRY

The manufacture of pigments is nearly as complex as the manufacture of the coatings. However, it is easy to divide this industry into three components, which are:

1. The manufacture of titanium dioxide by the sulfate process.
2. Manufacture of titanium dioxide by the chloride process.
3. Manufacture of other pigments by various processes.

While TiO_2 production by the chloride process probably exceeds that by the sulfate process today, the sulfate process will probably remain a significant factor for some time. Also, the problems inherent in the preparation of titanium dioxide pigments by the sulfate process appear to be more significant and difficult to control than those in the chloride process and development efforts should be concentrated in this area.

Unlike the sulfate process, there are a number of different chloride processes used in the manufacture of TiO_2. The large differences in emissions from the various type plant chlorinators should also be a subject of further study.

The R&D program in this industry should consist of the following steps:

1. Assemble all of the available information on the design basis used for the selection and sizing of existing electrostatic precipitators and scrubbers by contact with the manufacturers of titanium dioxide by the sulfate process, and by contact with the

manufacturers of air pollution control equipment.

2. Independent definition of the problem in terms of the physics and chemistry of the fume product and source test information established by the EPA.
3. Preparation of prototype specifications for a satisfactory control system by each means judged as a feasible approach, without regard to commercial duration of the process.
4. Economic evaluation of the alternatives judged feasible.
5. Selection of one (or possibly two) technically feasible alternatives for prototype development.
6. Small scale pilot testing of a prototype design.
7. Recommendations for full-scale testing.

The cost of the development program is likely to be large relative to the economic advantage achieved by any single pigment manufacturer by product recovery or air pollution control equipment cost reduction.

Estimates of the timing and costs can be divided into three phases. The first involves the investigatory and evaluation phase. This should require approximately 2000 man-hours of professional time and 1000 man-hours of non-professional time, and should cost on the order of $60,000. At the end of this phase, a feasible approach should have been selected and a pilot design prepared. The second phase involves the construction, field testing and evaluation of a prototype pilot unit. This is expected to involve an additional 1500 man-hours of professional time, 1500 man-hours of non-professional time and a lump sum cost for fabrication of the pilot unit of $25,000. The manpower costs are estimated to be approximately $50,000, for a total cost of $68,000.

The final phase, which is a preparation for the testing of a full-scale prototype, involves the design of a full-scale prototype and a good estimate of the installation and operating cost of the prototype. This phase is estimated to require approximately 1200 professional man-hours, 100 non-professional man-hours and to cost approximately $30,000.

The installation and operation of a full-scale prototype unit may be emitted from the research and development program proposed, and some cost-sharing arrangement worked out with a titanium dioxide manufacturer so that the principal costs of installation and operation are borne by the commercial process. The development costs could reasonably be funded by the public through the EPA.

The second area identified for research and development work is that of treatment of the flue gas discharged from the pigment digester. An alternative course of action involves the modification of the digestion process such that little or no gas is vented to the atmosphere. This has been judged to be less likely of success because of the large investment in existing sulfate process digesters in the industry. However, should a good approach to process modifications be proposed within the industry, direct funding of all or a part of the development work would be appropriate.

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LIST OF STANDARD ABBREVIATIONS

actual cubic feet per minute	ACFM
atmospheres gage (pressure)	atmg
British thermal units	Btu
centimeters	cm
change of pressure (delta pressure)	ΔP
change of temperature (delta temperature)	ΔT
cubic feet	ft^3
degrees Centigrade	°C
degrees Fahrenheit	°F
degrees Rankine	°R
diameter	dia
dollars	$
feet or foot	ft
gallon or gallons	gal
gallons per minute	gpm
grain or grains	gr
hour or hours	hr
hydrocarbon	Hcbn
inch or inches	in.
lower explosive limit	L.E.L.
meter or meters	m
milliliters	ml
millimeters	mm
millimeters of Mercury (pressure)	mmHg
millions (10^6)	MM
minute or minutes	min
mole	mol
non-volatile material	NVM
parts per million	ppm
per cent	%
pint or pints	pt
pound or pounds	lb
pounds per square inch gauge	psig
quart or quarts	qt
seconds	sec
square feet	ft^2
standard cubic feet	SCF
standard cubic feet per minute	SCFM
temperature	Temp
ton or tons	ton
water column (pressure)	w.c.
weight percent	wt.%
year or years	yr

APPENDIX A -1

MODEL PLANT COST DETAIL

APPENDIX A

MODEL PLANT COST DETAIL

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
101 - **Pebble Mill**			
Abbe - Model 8½ - 21" O.D. x 28" LG. Jacketed Mill with Burrstone lining complete with 3/4 HP motor & magnetic brake	1	3,600	
Ni-Hard Balls		100	
Electrical Wiring		1,700	
Foundation & Supports		500	
Installation		400	
Total		6,300	6,300
102 - **Pebble Mill**			
Abbe - Model 8B - 24" O.D. x 36" LG. Jacketed Mill with Burrstone lining complete with 1½ HP motor & magnetic brake	1	4,250	
Ni-Hard Balls		150	
Electrical Wiring		1,700	
Foundation & Supports		800	
Installation		500	
Total		7,400	7,400
103 - **Pebble Mill**			
Abbe - Model 6 - 32" O.D. x 36" LG. Jacketed Mill with Burrstone lining complete with 3 HP motor & magnetic brake	1	5,600	
Ni-Hard Balls		450	
Electrical Wiring		1,700	
Foundation & Supports		1,100	
Installation		600	
Total		9,450	9,450

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
104 - **Pebble Mill**			
Abbe - Model 5B - 42" O.D. x 48" LG. Jacketed Mill with Burrstone lining complete with 5 HP motor & magnetic brake	1	7,350	
Ni-Hard Balls		550	
Electrical Wiring		1,700	
Foundation & Supports		2,200	
Installation		800	
Total		12,600	12,600
105 - **Pebble Mill**			
Abbe - Model 2 - 60" O.D. x 48" LG. Jacketed Mill with Burrstone lining complete with 15 HP motor & magnetic brake	1	11,200	
Ni-Hard Balls		1,100	
Electrical Wiring		1,800	
Foundation & Supports		4,700	
Installation		1,300	
Total		20,100	20,100
106 - **Pebble Mill**			
Abbe - Model 2B - 60" O.D. x 72" LG. Jacketed Mill with Burrstone lining complete with 20 HP motor & magnetic brake	1	12,900	
Ni-Hard Balls		1,650	
Electrical Wiring		1,800	
Foundation & Supports		5,700	
Installation		1,500	
Total		23,550	23,550

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
107 - Pebble Mill			
Abbe - Model 0 - 72" O.D. x 96" LG. Jacketed Mill with Burrstone lining complete with 30 HP motor & magnetic brake	1	19,700	
Ni-Hard Balls		3,200	
Electrical Wiring		2,150	
Foundation & Supports		10,800	
Installation		2,300	
Total		38,150	38,150
Total unadjusted cost for Pebble Mills			117,550
Chicago area adjustment	4%		
Adjustment from Jan. to Dec. '72	5%		
Total	9%		10,600
Total installed cost for Pebble Mills			128,150

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
108 - Ball Mill			
Abbe - Model 6 - 32" O.D. x 36" LG. Jacketed Mill with Burrstone lining complete with 5 HP motor and magnetic brake	1	6,000	
Ni-Hard Balls		650	
Electrical Wiring		1,700	
Foundation & Supports		1,500	
Installation		700	
Total		10,550	10,550
109 - Ball Mill			
Epworth - 4'x5' Ball Mill manufactured in accordance with Sherwin-Williams specifications complete with 15 HP motor reducer drive	1	13,150	
Ni-Hard Balls		2,500	
Electrical Wiring		1,800	
Foundation & Supports		4,700	
Installation		1,700	
Total		23,850	23,850
Total unadjusted cost for Ball Mills			34,400
Adjustment - 9%			3,100
Total installed cost for Ball Mills			37,500

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
110 - Sand Mill			
Standard "Red Head" Mill Model 3P complete with 10 HP motor, feed pump and two charges of sand	1	3,350	
Electrical Wiring		1,800	
Foundations & Supports		300	
Installation		500	
Total		5,950	5,950
111 - Sand Mill			
Standard "Red Head" Mill Model 8P complete with 20 HP motor, feed pump, discharge pump and two charges of sand	1	5,100	
Electrical Wiring		1,800	
Foundations & Supports		600	
Installation		700	
Total		8,200	8,200
112 - Sand Mill			
Standard "Red Head" Mill Model 16P complete with 30 HP motor, feed pump, discharge pump and two charges of sand	1	6,300	
Electrical Wiring		2,150	
Foundations & Supports		900	
Installation		800	
Total		10,150	10,150
Total unadjusted cost for Sand Mills			24,300
Total adjusted cost for Sand Mills			26,500

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
113 - High Speed Disperser			
Morehouse Cowles - Model 515 VHV - Disperser complete with 10 HP explosion-proof motor	2	3,300	
Electrical Wiring		1,800	
Installation		400	
Total		5,500	11,000
114 - High Speed Disperser			
Morehouse Cowles - Model 520 VHV - Disperser complete with 25 HP explosion-proof motor	1	4,550	
Electrical Wiring		2,000	
Installation		500	
Total		7,050	7,050
115 - High Speed Disperser			
Morehouse Cowles - Model 720 VHV - Disperser complete with 50 HP explosion-proof motor	1	7,050	
Electrical Wiring		2,500	
Installation		800	
Total		10,350	10,350
116 - High Speed Disperser			
Morehouse Cowles - Model 1030 VHV - Two Speed Disperser complete with 100 HP explosion-proof motor	1	8,400	
Electrical Wiring		3,300	
Installation		1,000	
Total		12,700	12,700
Total unadjusted costs for High Speed Dispersers			41,100
Adjustment			3,700
Total installed costs for High Speed Dispersers			44,800

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
117 - Mixing Tanks			
Portable tank, 220 gallon capacity, 42" I.D. x 34" straight side with flat bottom mounted on 6" heavy duty casters; lift hooks with 2" half coupling outlet Carbon steel construction	20	350	7,000
118 - Finishing Tanks			
Floor mounted 550 gallon tank, 4' I.D. x 6' straight side with dished bottom and flat top complete with 3 HP top mounted agitator carbon steel	14	2,900	
Electrical Wiring		1,700	
Installation		300	
Total		4,900	68,600
119 - Finishing Tanks			
Floor mounted 1100 gallon tank, 5' I.D. x 8' straight side with dished bottom and flat top complete with 7½ HP top mounted agitator Carbon steel construction	8	4,500	
Electrical Wiring		1,700	
Installation		400	
Total		6,600	52,800
120 - Finishing Tanks			
Floor mounted 2200 gallon tank, 7' I.D. x 8' straight side with dished bottom and flat top complete with 15 HP top mounted agitator Carbon steel construction	3	5,700	
Electrical Wiring		1,800	
Installation		600	
Total		8,100	24,300
Total unadjusted cost for Mixing and Finishing Tanks			152,700
Adjustment			13,750
Total installed costs for Mixing and Finishing Tanks			166,450

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
121 - Filter			
Cuno - Model - FH-530-CW with support assembly. Carbon steel construction	1	200	
Installation		50	
Total		250	250
122 - Filter			
Cuno Micro Klean Filter with 6 cartridges. Carbon steel construction	3	655	
Installation		75	
Total		730	2,190
123 - Screens			
Lehman Vorti Sieve	2	3,000	
Support Cart		500	
Electrical Wiring		1,700	
Installation		300	
Total		5,500	11,000
124 - Can Filler			
Ambrose Model PF-9 Filling and sealing machine	2	10,000	
Lid Dropper & Can Closer		1,500	
Installation		1,000	
Total		12,500	25,000
125 - Bail-O-Matic			
Bail-O-Matic - Model "A"	1	16,000	
Electrical Wiring		1,700	
Installation		1,000	
Total		18,700	18,700
126 - Barrel Filler			
Mantes - Model 16 MTFF Barrel Filler	1	4,500	
Installation		400	
Total		4,900	4,900

Item		Quan.	Unit Cost	Total
Equipment - Paint Plant				
127 - Labeler				
New Way Labeler - Model "EP"		1	6,000	
Electrical Wiring			1,700	
Installation			500	
	Total		8,200	8,200
128 - Packing Station				
New Way Model EC Caser		1	9,550	
Electrical Wiring			100	
Installation			1,000	
	Total		10,600	10,600
129 - Case Sealer				
New Way Model F-20 Kiwi		1	7,000	
Kiwi Carton Coder			300	
Electrical Wiring			1,700	
Installation			1,000	
	Total		10,000	10,000
130 - Carton Stencil		1	500	500
131 - Portable Pumps and Carts		2	2,500	5,000
Total Filling and Packaging Equipment Adjusted Cost				96,340
Adjustment				8,660
Total Installed Cost for Filling and Packaging Equipment				105,000

Item	Quan.	Unit Cost	Total
Equipment - Paint Plant			
Laboratory Equipment			
Viscometers	4	250	1,000
Spray Booth - Binks Model PBFL-4			
Electrical Wiring	2	475	
Installation	4	1,700	
Installation		125	
Total		2,300	4,600
Drying Oven - "Blue M" Model OV-472A-2 with floor stand	2	550	
Electrical Wiring		1,700	
Installation		150	
Total		2,400	4,800
Tables, Benches & Disks			2,000
Total Unadjusted Cost for Laboratory Equipment			12,400
Adjustment			1,100
Total Installed Cost for Laboratory Equipment			13,500

Item	Quan.	Unit Cost	Total
Equipment - Resin Plant			
201 - 500 Gallon Resin Reactor Unit	1	55,300	
Complete with:			
Agitator & Baffles			
Cooling Coil			
Baffles			
Fume Scrubber			
Spray Tower			
Ejector			
Circulating Pump			
1000 Gallon Thinning Tank			
Thinning Tank Agitator			
Thinning Tank Scale			
Thinning Tank Condenser			
Control Panel			
Material of Construction Stainless Steel			
Quotation from Brighton Corporation Cincinnati, Ohio			
Electrical Wiring		5,000	
Piping - included in the above quotation			
Installation		11,000	
Structural Steel		3,000	
Insulation		1,800	
Total		76,100	76,100

Item	Quan.	Unit Cost	Total
Equipment - Resin Plant			
202 - 1500 Gallon Resin Reactor Unit Complete with:	1	85,400	
Agitator			
Inconel Dimpled Jacket			
Sampler			
Baffles			
Cooling Coil			
Partial Condenser			
Total Condenser			
Decanter-Receiver			
Vacuum System			
Fume Scrubber			
Spray Tower			
Ejector			
Circulating Pump			
3000 Gallon Thinning Tank			
Thinning Tank Agitator			
Thinning Tank Scale			
Thinning Tank Condenser			
Control Panel			
Material of Construction Stainless steel unless specified otherwise			
Quotation from Brighton Corp. Cincinnati, Ohio			
Electrical Wiring		8,500	
Piping - included in the above quotation			
Installation		17,000	
Total		110,900	110,900

Item	Quan.	Unit Cost	Total
Equipment - Resin Plant			
203 - Filter Feed Pumps	2	600	
Viking Model K-124 Cast Iron			
Electrical Wiring		1,700	
Foundations & Supports		200	
Installation		100	
Total		2,600	5,200
204 - Resin Transfer Pump			
Viking Model K-124 Cast Iron	2	600	
Electrical Wiring		1,700	
Foundations & Supports		200	
Installation		100	
Total		2,600	5,200
205 - Filter Presses			
Shriver - 18" x 18" Filter Press with 70 ft^2 of filtering area Cast iron with "Hydrd Kloser"	2	2,000	
Installation		200	
Total		2,200	4,400
206 - Relief Tank			
1500 Gallon - Carbon Steel	1	1,400	
Foundations & Supports		600	
Installation		300	
Total		2,300	2,300
Total Unadjusted Cost for Resin Plant			204,100
Total Adjusted Cost for Resin Plant			222,500

Item	Quan.	Unit Cost	Total
Equipment - Storage Area			
301 - Odorless Mineral Spirits Stg. Tank			
25,000 Gallons - Carbon Steel	1	11,200	
Installation		1,300	
Total		12,500	12,500
302 - Odorless Mineral Spirits Transfer Pump			
Goulds - 1 x 2 x 10 - Carbon Steel Pump complete with 3 HP motor	1	700	
Electrical Wiring		1,700	
Installation		100	
Piping		3,250	
Tokheim - 1½" Line Meter		750	
Total		6,500	6,500
303 - Industrial Alkyd Solvent Stg. Tank			
25,000 Gallons - Carbon Steel	1		12,500
304 - Industrial Alkyd Solvent Transfer Pump			
Goulds - 1 x 2 x 10 - Carbon Steel Pump complete with 3 HP motor	1	700	
Electrical Wiring		1,700	
Installation		100	
Piping		3,250	
Tokheim - 1½" Line Meter		750	
Total		6,500	6,500
305 - Waste Solvent Tank			
1,000 Gallons - Carbon Steel	2	1,200	
Installation		300	
Total		1,500	3,000
Pump - Goulds - 1 x 2 x 10 - Carbon Steel with 3 HP motor	1	700	
Installation		100	
Electrical Wiring		1,700	
Piping		2,000	
Total		4,500	4,500

Item	Quan.	Unit Cost	Total
Equipment - Storage Area			
306 - Aqueous Waste Tank			
1,000 Gallons - Carbon Steel	1	1,200	
Installation		300	
Pump - Goulds - 1 x 2 x 10	1	800	
Electrical Wiring		1,700	
Piping		600	
Total		4,500	4,500
307 - Industrial Alkyd Tank			
1,000 Gallons - Carbon Steel Tank with Pump & Meter	4	5,250	21,000
308 - Interior Latex Tank			
22,500 Gallons - Stainless Steel	1	15,000	
Installation		1,000	
Pump - Viking Model K-124 Stainless Steel with Motor	1	1,700	
Installation		100	
Tokheim Meter - 1½" Stainless Steel		2,500	
Electrical Wiring		1,700	
Piping - 304 Stainless Steel		1,100	
Total		23,100	23,100
309 - Exterior Latex Tank			
17,500 Gallons - Stainless Steel	1	13,500	
Installation		800	
Pump - Viking Model K-124 Stainless Steel complete with 3 HP Motor	1	1,700	
Installation		100	
Tokheim Meter - 1½" Stainless Steel		2,500	
Electrical Wiring		1,700	
Piping - 304 Stainless Steel		1,100	
Total		21,400	21,400

Item	Quan.	Unit Cost	Total
Equipment - Storage Area			
310 - Oil Storage Tank			
12,500 Gallons - Carbon Steel	2	6,300	
Installation		700	
Pump - Viking Model K-124 Carbon Steel complete with 3 HP motor		550	
Installation		100	
Tokheim Meter - 1½" Carbon Steel		750	
Electrical Wiring		1,700	
Piping - Carbon Steel		600	
Total		10,700	21,400
311 - Industrial Alkyd Storage Tank			
10,000 Gallons - Carbon Steel	1	5,500	
Installation		600	
Pump - Viking Model K-124		550	
Installation		100	
Tokheim Meter - 1½" Carbon Steel		750	
Electrical Wiring		1,700	
Piping - Carbon Steel		600	
Total		9,800	9,800
312 - Industrial Alkyd Storage Tank			
7,500 Gallons - Carbon Steel	1	4,600	
Installation		500	
Pump - Viking Model K-124		650	
Tokheim Meter - 1½" Carbon Steel		750	
Electrical Wiring		1,700	
Piping - Carbon Steel		600	
Total		8,800	8,800

Item	Quan.	Unit Cost	Total
Equipment - Storage Area			
313 - Trade Alkyd Tank			
10,000 Gallons - Carbon Steel	1	9,800	9,800
314 - Trade Alkyd Tank			
5,000 Gallons - Carbon Steel	1	3,400	
Installation		400	
Pump - Viking Model K-124		650	
Tokheim Meter - 1½" Carbon Steel		750	
Electrical Wiring		1,700	
Piping		600	
Total		7,500	7,500
315 - Glycerine Storage Tank			
7,500 Gallons - Carbon Steel Installation, Pump, Piping, Wiring and Meter	1	8,800	8,800
316 - Portable Pumps with Carts	3	2,500	7,500
Tank Gauges	20	250	5,000
Total Storage Area Unadjusted Cost			194,100
Adjustment			17,500
Total Storage Area Cost			211,600

Item	Quan.	Unit Cost	Total
Equipment - Miscellaneous			
Scales - 0-100 lbs.	3	200	600
0-500 lbs.	2	250	500
Ford Trucks			
Electric - 4,000 lb. Capacity	1	9,350	
Charger		250	
Total		9,600	9,600
I.C. Engine - 4,000 lb. Capacity	2	7,300	14,600
Racks			
4' wide - 2' deep	6,250 ft^2		9,400
Fire Extinguishers			2,200
Emergency Lighting			22,500
Furniture			
Office		5,000	
Lunch Room		2,500	
Locker Room		1,500	
Total		9,000	9,000
Drum and Hand Pallet Trucks		1,500	1,500

Item	Quan.	Unit Cost	Total
Equipment - Miscellaneous			
Shop Equipment			
Cabinets & Shelves		3,000	
Grinders		1,900	
Press		3,000	
Radial Drill		12,000	
Wells Saw		1,800	
Milling Machine		3,600	
Lathe		25,000	
Benches		850	
Vises		700	
Welding Machines		900	
Band Saw		2,100	
Hand Brake		1,800	
Roller		2,200	
Shearer		1,200	
Hand Tools		1,000	
Total		61,050	61,050
Total Unadjusted Cost for Miscellaneous Equipment			130,950
Adjustment			11,800
Total Cost for Miscellaneous Equipment			142,750

Item	Quan.	Unit Cost	Total
Utilities			
Dowtherm System			
Two Million Btu/hr Direct Fired Heater - Carbon Steel	1	36,000	
Piping		5,500	
Insulation		2,800	
Electrical Wiring		2,500	
Total		46,800	46,800
Inert Gas Generator			
Kemp - Model 6 - PH - 5000 CFH Inert Gas System	1	23,100	
Storage Tank		1,200	
Installation		2,500	
Electrical Wiring		2,150	
Piping		4,600	
Total		33,550	33,550
Compressed Air			
150 CFM Packaged Air Compressor complete with 50 HP Motor	1	3,500	
Electrical		2,500	
Installation		1,000	
Piping		5,200	
Total		12,200	12,200
Cooling Water			
6" Sch. 40 Carbon Steel		11,000	
4" Sch. 40 Carbon Steel		7,000	
3" Sch. 40 Carbon Steel		2,520	
2" Sch. 40 Carbon Steel		1,950	
1½" Sch. 40 Carbon Steel		1,000	
1" Sch. 40 Carbon Steel		975	
3/4" Sch. 40 Carbon Steel		600	
½" Sch. 40 Carbon Steel		275	
Sub-Total		25,320	
Insulation		500	
Total		25,820	25,820

Item	Quan.	Unit Cost	Total
Utilities			
Portable Water			
Piping		950	
Hot Water Heaters		800	
Electrical Wiring		3,400	
Total		5,150	5,150
Sewers & Drains			
Process - Piping		7,150	
Catch Basins		2,000	
Intercepter		1,500	
Sanitary - Piping		6,650	
Catch Basins		4,000	
Total		21,300	21,300
Natural Gas			
Piping			7,350
Grounding			
Allowance			10,000
Telephones			1,500
Total Unadjusted Cost for Utilities			163,670
Adjustment			14,730
Total Cost for Utilities			178,400
Building Summary			
Sitework		167,100	
Part I - Raw Material Warehouse		219,700	
Part II - Manufacturing Arch		912,450	
Part III - Finished Goods Warehouse		526,700	
Total		1,825,950	1,825,950

SITE WORK

Item	Quan.	Unit Cost	Total Material
Strip Top Soil (8")	2,080 C.Y.	.65	1,350
Excavation	3,560 C.Y.	1.36	4,850
Compacted Fill	5,640 C.Y.	8.90	50,100
Asphalt Paving, Base Course, Grading	6,200 S.Y.	4.20	26,000
Fence (8' Chain Link, w/barb wire)	620 L.F.	5.00	3,100
Utility Building	2,000 S.F.	8.00	16,000
Drum Storage Pad (6" conc.)	9,000 S.F.	.80	7,200
Tank Farm Pad (6" conc.)	2,400 S.F.	.80	1,900
Tank Farm Dike	200 L.F.	37.00	7,400
Seeding	48,000 S.F.	.05	2,400
Landscaping	L.S.	2,000	2,000
Exterior Lighting	6	400	2,400
			124,700

Contractors - Overhead & Profit	- 25%	
Chicago Area Adjustment	- 4%	
Adjustment from Jan. to Dec. '72	- 5%	
	34%	42,400
Total		167,100

PART I - RAW MATERIAL WAREHOUSE

Item	Quan.	Unit Cost	Total Material
Excavation	630 C.Y.	1.36	850
Foundations	90 C.Y.	90	8,100
Compacted Fill	230 C.Y.	8.90	2,050
First Floor (6" conc.)	17,000 S.F.	.80	13,600
Roof Deck, Insulation & Roofing	17,000 S.F.	.81	13,800
Structural Steel	145,000 #	.22	32,000
Insulated Sandwich Panel	9,000 S.F.	2.35	21,200
Partition Walls (8" Block)	1,100 S.F.	1.75	1,950
Gravel Stop	570 L.F.	1.30	750
Roof Drains & Piping	2 ea.	700	1,400
Smoke Vents	6 ea.	880	5,300
Doors (3' x 7')	5 ea.	265	1,300
Doors (8' x 8') w/operator 510 + 465	6 ea.	975	5,850
Dock Levelers	6 ea.	1,100	6,600
Dock Seals	6 ea.	600	3,600
Dock Canopy	1,000 S.F.	3.00	3,000
Dock Stairway	1 ea.	1,000	1,000
Ceilings	900 S.F.	1.00	900
V.A. Tile	900 S.F.	.50	450
Toilet Fixtures	7 ea.	400	2,800
Toilet Partitions & Screens	4 ea.	100	400
Paint	2,200 S.F.	.20	450
Heat & Vent	17,000 S.F.	.75	12,800
Lighting	17,000 S.F.	.90	15,300
Sprinklers (ord. hazard)	17,000 S.F.	.50	8,500
			163,950
Contractors - Overhead & Profit	- 25%		
Chicago Area Adjustment	- 4%		
Adjustment from Jan. to Dec.'72	- 5%		
	34%		55,750
Total			219,700

PART I - RAW MATERIAL WAREHOUSE

Item	Quan.	Unit Cost	Total Material
Excavation	630 C.Y.	1.36	850
Foundations	90 C.Y.	90	8,100
Compacted Fill	230 C.Y.	8.90	2,050
First Floor (6" conc.)	17,000 S.F.	.80	13,600
Roof Deck, Insulation & Roofing	17,000 S.F.	.81	13,800
Structural Steel	145,000 #	.22	32,000
Insulated Sandwich Panel	9,000 S.F.	2.35	21,200
Partition Walls (8" Block)	1,100 S.F.	1.75	1,950
Gravel Stop	570 L.F.	1.30	750
Roof Drains & Piping	2 ea.	700	1,400
Smoke Vents	6 ea.	880	5,300
Doors (3' x 7')	5 ea.	265	1,300
Doors (8' x 8') w/operator 510 + 465	6 ea.	975	5,850
Dock Levelers	6 ea.	1,100	6,600
Dock Seals	6 ea.	600	3,600
Dock Canopy	1,000 S.F.	3.00	3,000
Dock Stairway	1 ea.	1,000	1,000
Ceilings	900 S.F.	1.00	900
V.A. Tile	900 S.F.	.50	450
Toilet Fixtures	7 ea.	400	2,800
Toilet Partitions & Screens	4 ea.	100	400
Paint	2,200 S.F.	.20	450
Heat & Vent	17,000 S.F.	.75	12,800
Lighting	17,000 S.F.	.90	15,300
Sprinklers (ord. hazard)	17,000 S.F.	.50	8,500
			163,950

Contractors - Overhead & Profit	- 25%	
Chicago Area Adjustment	- 4%	
Adjustment from Jan. to Dec.'72	- 5%	
	34%	55,750
Total		219,700

PART II - MANUFACTURING AREA

Item	Quan.	Unit Cost	Total Material
Excavation	1,100 C.Y.	1.36	1,500
Foundations	280 C.Y.	90	25,200
Compacted Fill	820 C.Y.	8.90	7,300
First Floor (6" conc.)	22,000 S.F.	.80	17,600
Second Floor (6" conc.)	22,000 S.F.	2.00	44,000
Roof (8" Flexicore)	22,000 S.F.	1.65	36,300
Roof Insulation & Roofing	22,000 S.F.	.46	10,100
Structural Steel	570,000 #	.23	131,000
Walls (8" Block & 4" Brick)	3,600 S.F.	3.25	11,700
Walls (8" Conc. Block)	6,100 S.F.	1.75	10,700
Coping	620 L.F.	3.25	2,000
Flashing	620 L.F.	.80	500
Windows	880 S.F.	7.00	6,200
Roof Drains & Piping	2 ea.	700	1,400
Smoke Vents (4' x 8')	14 ea.	880	12,300
Doors (3' x 7')	10 ea.	265	2,650
Doors (8' x 8') w/operator	5 ea.	975	4,900
Fire Proof Structural Steel	52,000 S.F.	2.10	109,500
Paint Walls	53,000 S.F.	.20	10,600
Heat and Vent	44,000 S.F.	2.10	92,500
Lighting	44,000 S.F.	1.60	70,500
Sprinklers (call system)	44,000 S.F.	.75	33,000
Walls (12" Conc. Block)	16,800 S.F.	2.35	39,500
			680,950

Contractors - Overhead & Profit	- 25%	
Chicago Area Adjustment	- 4%	
Adjustment from Jan. to Dec. '72	- 5%	
	34%	231,500
Total		912,450

PART III - FINISHED GOODS WAREHOUSE

Item	Quan.	Unit Cost	Total Material
Excavation	580 C.Y.	1.36	800
Foundations	80 C.Y.	90	7,200
Compacted Fill	500 C.Y.	8.90	4,450
First Floor (6" conc.)	45,000 S.F.	.80	36,000
Roof Deck, Insulation & Roofing	45,000 S.F.	.81	36,400
Structural Steel	382,000 lb.	.22	84,000
Insulated Sandwich Panel	15,600 S.F.	2.35	36,700
Partition Walls	4,800 S.F.	1.75	8,400
Gravel Stop & Fascia	850 L.F.	1.30	1,100
Roof Drains	4 ea.	700	2,800
Smoke Vents	14 ea.	880	12,300
Doors (3' x 7')	11 ea.	265	2,900
Doors (8' x 8') w/operator	9 ea.	975	8,800
Dock Levelers	9 ea.	1,100	9,900
Dock Seals	9 ea.	600	5,400
Dock Canopy	1,500 S.F.	3.00	4,500
Dock Stairway	1 ea.	1,000	1,000
Ceilings	6,800 S.F.	1.00	6,800
V.A. Tile	6,800 S.F.	.50	3,400
Toilet Fixtures	20 ea.	400	8,000
Toilet Partitions & Screens	9 ea.	100	900
Lockers	70 ea.	40	2,800
Heat & Vent	45,000 S.F.	.75	34,000
Lighting	45,000 S.F.	.90	40,500
Sprinklers (Calc. Syst.)	45,000 S.F.	.75	34,000
			393,050

Contractors - Overhead & Profit	- 25%	
Chicago Area Adjustment	- 4%	
Adjustment from Jan. to Dec. '72	- 5%	
	34%	133,650
Total		526,700

APPENDIX B-1

PROCESS NARRATIVE OF PAINT AND VARNISH INDUSTRY

APPENDIX B

PROCESS NARRATIVE OF PAINT AND VARNISH INDUSTRY

The Paint and Varnish industry is one of the oldest manufacturing industries in the United States. The industry is made up of about 1,600 companies operating 1,875 plants.(1) It is well distributed geographically throughout the country and the number of plants or production volume is definitely related to density of population. Even though about 27 companies account for about 57% of the total sales, the industry is one of the few remaining which contains numerous small companies that specialize in a limited product line to be marketed within a geographical region. There are fewer than 20 companies that sell paint nationwide.

The industry is now emerging as a scientific business from its beginning as an art 50 years ago. Even with rapid growth in technology, the industry processing techniques still are not well defined and vary from one producer to another. To add further complication, the industry is technically one of the most complex of the chemical industry. A plant that produces a broad line of products might utilize over 600 different raw materials and purchased intermediates. These materials can be generally classified in the following categories: oils, metallic driers, resins, pigment extenders, plasticizers, solvents, dyes, bleaching agents, organic monomers for resins and additives of many kinds.

The industry produces an equally large number of finished products which are generally classified as trade sale finishes, maintenance finishes and industrial finishes.

Trade sale products are stock-type paints generally distributed through wholesale-retail channels and packaged in sizes ranging from 1/2 pint to 1 gallon. A subdivision of trade sale products are maintenance finishes which are used for the protection and upkeep of factories, buildings and structures such as bridges and storage tanks. Since they are usually stock type, they come under the Department of Commerce definition of trade sales.

The other major type of paint products are industrial finishes which are generally defined as those applied to manufactured products. These finishes such as automotive, aircraft, furniture and electrical are usually specifically formulated for the using industry. Within these major product lines there are literally thousands of different products for many different applications and types of customers. Trade sales finishes and industrial finishes are produced in almost equal volume with the production for this year estimated at 475 million gallons for each type. Trade sales, however, are expected to account for 55% of the dollar sales or about $1,685 million dollars.

PROCESS DESCRIPTION

Starting with all purchased raw material, the manufacturing process for pigmented products is deceptively simple from a process viewpoint. Basically, it consists of mixing or dispersing pigment and vehicle to give the final product. This is schematically illustrated in Figure 1.

The paint vehicle is defined as the liquid portion of the paint and consists of volatile solvent and non-volatile binder such as oils and resins. The non-volatile portion is also called the vehicle solid or film former. The pigment portion of the paint consists of hiding pigments such as titanium dioxide (TiO_2), extenders or fillers such as talc or barium sulfate, and any mineral matter used for flatting or other purposes.

The incorporation of the pigment in the paint vehicle is accomplished by a combination of grinding and dispersion or dispersion alone. When it is necessary to further grind the raw pigment, the pebble or steel ball mills are normally used. With the advent of fine particle grades of pigment and extenders, as well as the wide spread use of wetting agents, the trend is toward milling methods that are based on dispersion without grinding. This dispersion consists of breakup of the pigment clusters and agglomerates, followed by wetting of the individual particles with the binder or vehicle. Some of the more popular methods currently being used are high speed disc impellers, high speed impingement mills and the sand mill.

Aside from this dispersion step, pigment paint manufacturing involves handling of raw material as well as handling and packaging of finished product. Operations of a typical plant may be summarized as a raw material and finished product handling problem with a variety of interdispersed batch operations. The inter-relationship of all these operations is schematically illustrated in Figure 2. The operations depicted are those of a plant that makes its own resins and produces both trade sale and industrial finishes.

Many of the larger and some of the medium size manufacturers produce a significant amount of their formulation ingredients, including pigments, resins, modified oils and basic chemicals. Certain manufacturers produce these ingredients in an amount exceeding their requirements and sell the excess to other manufacturers. A significant number also produce only a portion of their resins and purchase the remainder from their competitors or suppliers who specialize in resin manufacturing.

The manufacturing of resins and varnishes is by far the most complex process in a paint plant, primarily as the result of the large variety of different raw materials, products and cooking formulas utilized. The complexity begins with the nomenclature used in classification of the final product. Originally, varnishes were all made from naturally occurring material and they were easily defined as a homogeneous solution of drying oils and resins in organic solvents. As new synthetic resins were developed, the resulting varnishes were classified as resins rather than varnishes. Examples of this are alkyd, epoxy and polyurethane resin varnishes.

There are two basic types of varnishes, spirit varnishes and oleoresinous varnishes. Spirit

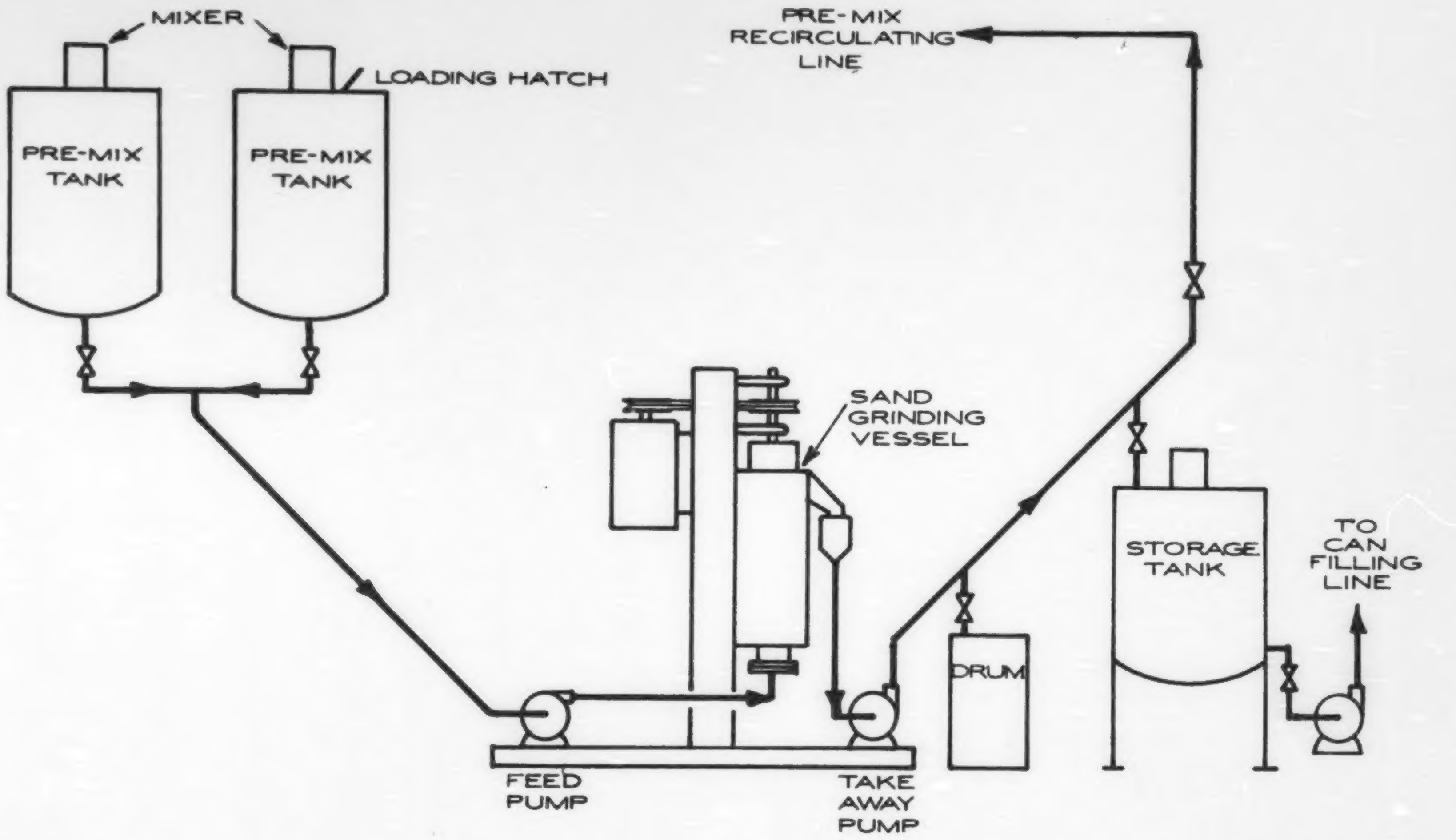
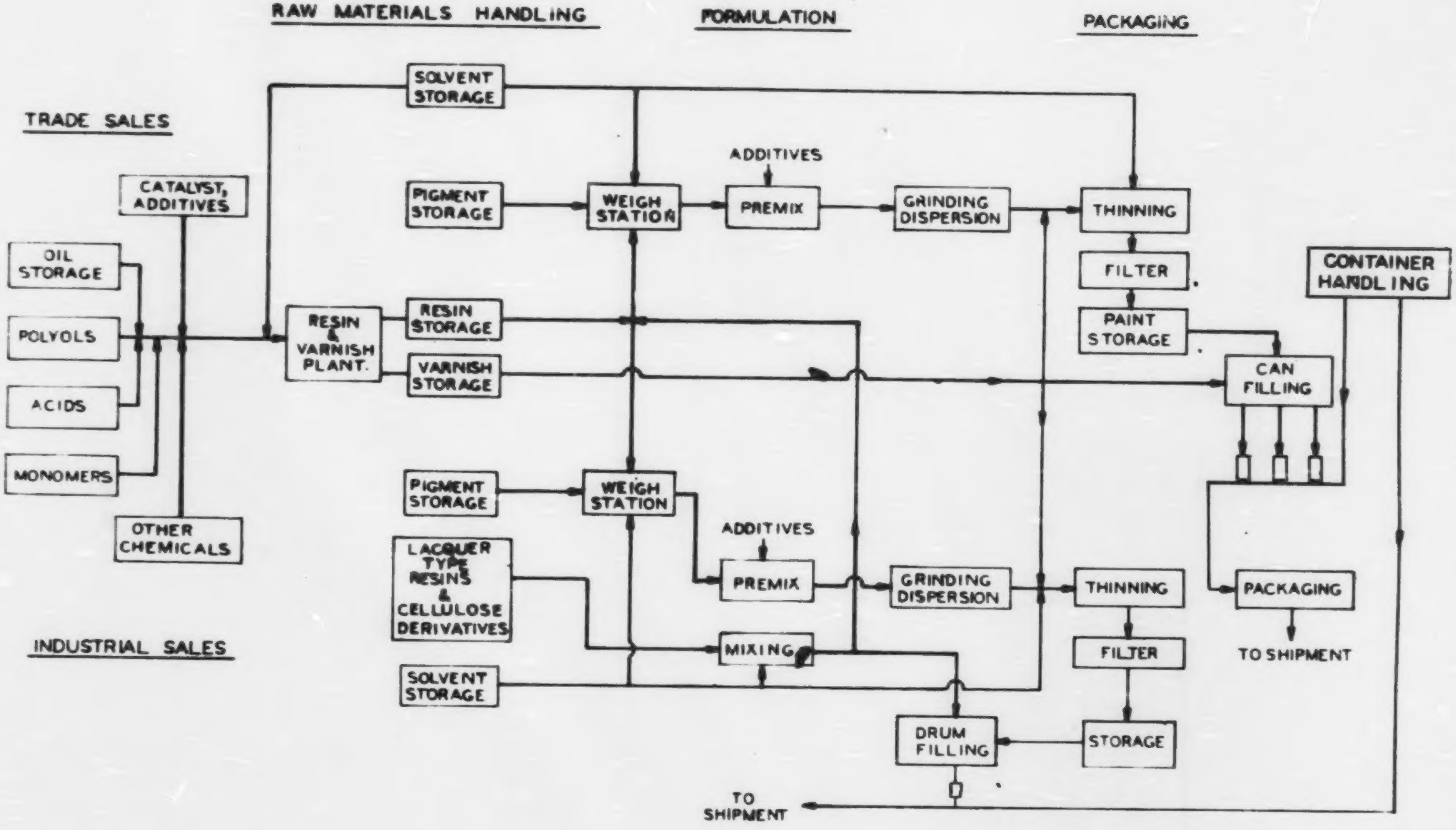


FIGURE 1

PAINT MANUFACTURING USING SAND MILL FOR GRINDING OPERATION

FIGURE 2

MATERIALS FLOW SHEET FOR PAINT MANUFACTURING



varnishes are formed by dissolving a resin in a solvent. They dry by solvent evaporation. Shellac is a good example of a spirit varnish. Another material that might fall in this category is lacquer. Technically, lacquers are defined as a colloidal dispersion or solution of nitro-cellulose, or of similar film-forming compounds, with resins and plasticizers, in solvent and diluents which dry primarily by solvent evaporation.

Oleoresinous varnishes, as the name implies, are solutions of both oils and resins. These varnishes dry by solvent evaporation and by reaction of the non-volatile liquid portion with oxygen in the air to form a solid film. They are classified as oxygen convertible varnishes and the film formed on drying is insoluble in the original solvent. A summary of the various types of material used in the production of classical varnishes is given in Table 1.

Varnish is cooked in both portable kettles and large reactors. Kettles are used only to a limited extent and primarily by the smaller manufacturers. The very old, coke fired, 30 gallon capacity copper kettles are no longer used. The varnish kettles which are used, have capacities of 150 to 375 gallons. These are fabricated of stainless steel, have straight sides and are equipped with three or four-wheel trucks. Heating is done with natural gas or fuel oil for better temperature control. The kettles are fitted with retractable hoods and exhaust pipes, some of which may incorporate solvent condensers. Cooling and thinning are normally done in special rooms. A typical varnish production operation is illustrated in Figure 3.

The manufacturing of oleoresinous varnishes is somewhat more complex than for spirit varnishes. This manufacture consists of the heating or cooking of oil and resins together for the purpose of obtaining compatability of resin and oil and solubility of the mixture in solvent, as well as for development of higher molecular weight molecules or polymers.

The time and temperature of the cook are the operating variables used to develop the desired end product polymerization or "body". The chemical reactions which occur are not well defined. The resin is a polymer before cooking and may or may not increase in molecular size during the cook. This resin may react with the oil to produce copolymers of oil and resin or it may exist as a homogeneous mixture or solution of oil homopolymers and resin homopolymers.

It is possible to blend resins and heat-bodied oil and obtain the same varnish that can be produced by cooking the resin and the unbodied oils. This indicates that copolymerization is not the fundamental reaction in varnish cooking.

Heat bodying or polymerization of an oil is done to increase its viscosity and is carried out in a kettle in a fashion similar to varnish cooking. The fundamental reaction that occurs is polymerization of the oil monomers to form dimers with a small portion of trimers.

There is a large variety of synthetic resins produced for use in the manufacture of surface coatings. A listing of the more popular resins is given below. They are listed by order of consumption by the coatings industry: (6)

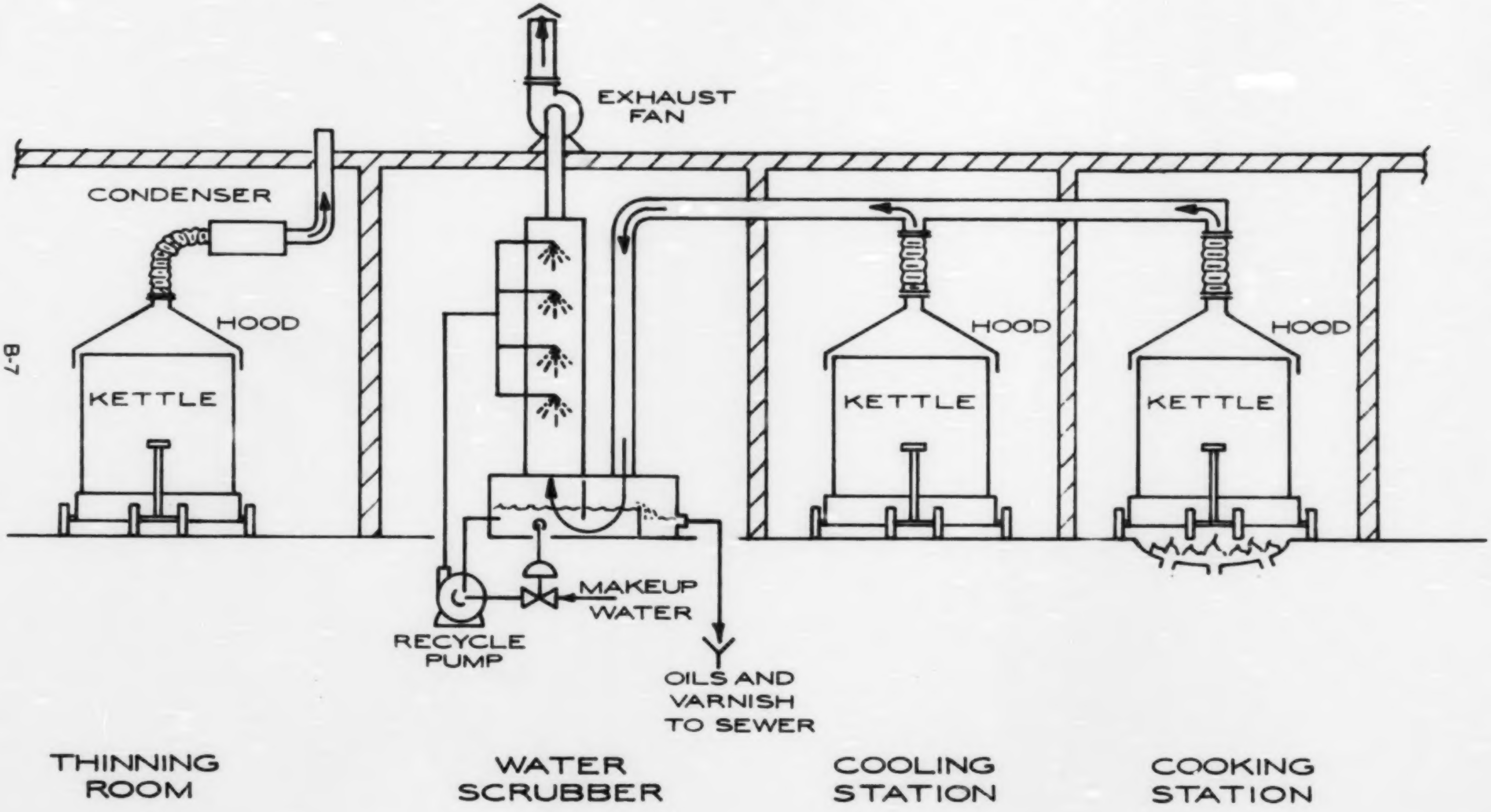
TABLE 1

VARNISH RAW MATERIAL[2]

OILS	RESINS	SOLVENTS	DRIERS	ADDITIVES
1. Hard	1. Natural	1. Mineral Spirits	Lead	Anti-Skinning Agents
a. Tung	a. Fossil resin, congo kauri, pontianak	2. VM&P Naphtha	Manganese	
b. Oiticica		3. Toluol	Cobalt	
c. Dehydrated castor oil	b. Semi-fossil resin manila, boea, batu, eastindia	4. Xylol	Calcium	Ultra-violet absorber
		5. Terpene Solvents	Zirconium	
2. Soft				
a. Linseed	c. Recent and crop resin dammar, accroides sandaral mastic, elemi, shellac			Flattening Agents
b. Safflower				
c. Soya				
d. Fish				
e. Tall oil fatty acids	d. Rosin			
	Gum rosin			
3. Chemically Modified	Wood rosin			
a. Maleic-treatment	Tall oil rosin			
	Rosin esters			
	2. Synthetic Resin			
	a. Maleic resin phenolic resin			
	3. Metallic Soaps			
	a. Limed rosin			
	b. Zinc resinate			

FIGURE 3

TYPICAL VARNISH COOKING ROOM



Alkyd
Vinyl
Amino
Epoxy
Acrylic
Styrene Butadiene
Phenolic
Polyester
Urethane
Silicone

By far the most widely used of these resins are the alkyds and the vinyls. Alkyd consumption is approximately five times that of the vinyl, which is approximately twice that of the amino resins. Further discussion will concentrate on alkyd resins.

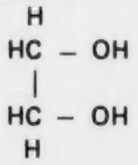
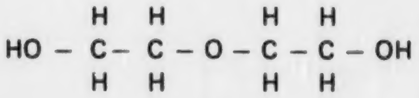
Alkyd resins comprise a group of synthetic resins which can be described as oil-modified polyester resins. They are produced from the reaction of polyols or polyhydric alcohol, polybasic acid and oil or fatty monobasic acid. A listing and discussion of commonly used raw materials will follow.

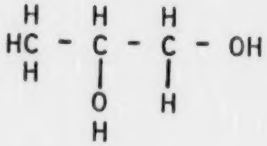
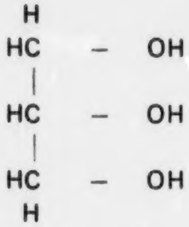
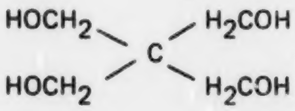
1. Oils or fatty acid (2)

Linseed
Soybean
Safflower
Tall Oil fatty acid
Tall Oil
Fish
Tung (minor)
Oiticica (minor)
Dehydrated Castor (minor)
Castor
Coconut
Cottonseed
Lauric Acid
Pelargonic Acid
Isodecanoic Acid

The materials in the first column are oxidizing or drying types. The materials in the second column are non-oxidizing and yield soft non-drying alkyds which are used primarily as plasticizers for hard film resins. The acids shown in this column are the only materials that are strictly synthetic in origin.

2. Polyols

Name	Formula	Form
Ethylene glycol	 $\begin{array}{c} H \\ HC - OH \\ \vert \\ HC - OH \\ H \end{array}$	Liquid
Diethylene glycol	 $HO - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - O - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - OH$	Liquid

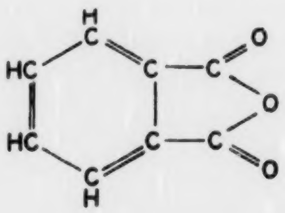
Propylene glycol	 $H\overset{H}{\underset{H}{C}} - \overset{H}{\underset{\substack{\vert\\O\\H}}{C}} - \overset{H}{\underset{\substack{\vert\\H}}{C}} - OH$	Liquid
Glycerine CP-95% glycerine Super-98%	 $\begin{array}{l}H\\HC - OH\\ \vert\\HC - OH\\ \vert\\HC - OH\\H\end{array}$	Liquid
Pentaerythritol		White Solid

Glycerol or glycerine was the first polyol used for alkyds. It is also the most widely used polyol for alkyds.

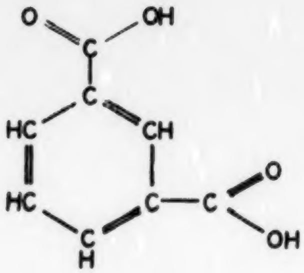
The second polyol, based on usage, is pentaerythritol (PE), which came into common use in the 1940's. PE is supplied as "technical grade" material and contains mono, di, tri and polypentaerythritol. The material consists primarily of the mono form which was illustrated previously in the list of polyols.

The important distinguishing feature of the various polyols is the number of potentially reactive hydroxyl groups in the molecule, known as functionality. The glycols with a functionality of two produce only straight chain polymers and their resins are soft and flexible. The resultant products are used primarily as plasticizers for hard resins. Glycerine has a functionality of three and is used primarily in short and medium oil alkyds. Pentaerythritol, with a functionality of four, cross-links to a greater extent, forming harder polymers. It is ideal for use in long oil alkyds.

3. Acids and Anhydrides

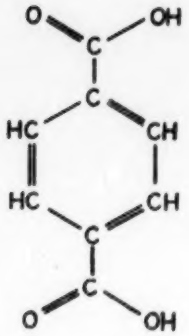
Name	Formula	Form
Phthalic anhydride (ortho)		White solid

Isophthalic
acid (meta)



White needles

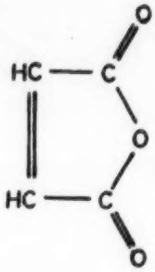
Terephthalic
acid (para)



White crystals

Maleic
anhydride

White solid

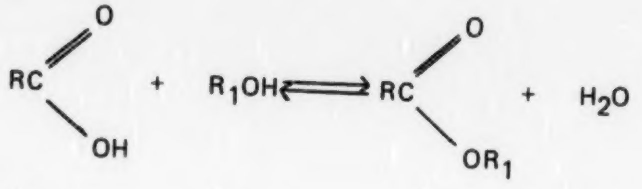


The acidic material can be used as an acid or anhydride. The anhydride is formed from two molecules of acid minus a molecule of water or removal of one molecule of water from a di acid. It is preferred, since it reacts faster and yields less water for removal from the cook.

For many years, phthalic anhydride (ortho) (PA) was the only polybasic acid used in substantial proportions in alkyds. It still remains the predominant dibasic acid. PA is produced from the catalytic oxidation of naphthalene or ortho-xylene.

The chemistry of alkyd resin systems is very complex. So much so that theoretical considerations offer only a good starting point. Final formulae and variations are developed by trial and error changes, based on performance requirements and shortcomings of previous batches.

Condensation is the reaction basic to all polyester resins, including alkyds. This reaction follows the elementary equation for esterification as shown below:



Acid + Alcohol (Ester + Water) ⟶

For Alkyd Resins

$$PA + Glycerine \rightleftharpoons Ester + H_2O$$

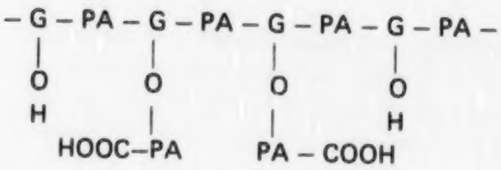
The ester monomer formed is very complex and further reacts to form large polymers called resins. The polymers formed are low in molecular weight by comparison to other resins. For example alkyd resins have molecular weights ranging from 1,000 to 7,000 while some vinyl and acrylic resins have average molecular weights in excess of 100,000 and in some cases as high as 500,000.

The alkyd polymers also react with oil or fatty acid and are generally classified by the amount of oil or PA used in the formulation, as described below:

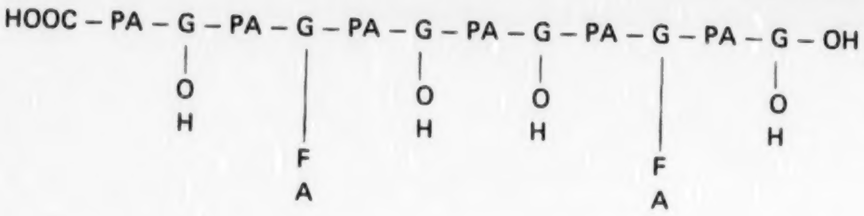
	% Oil	% PA
Short Oil	33 to 45	35
Medium Oil	46 to 55	30 to 35
Long Oil	56 to 70	20 to 30
Very Long Oil	71 up	20

The resulting reactants of the PA, polyol and oil may be represented in part as shown below.

Phthalic Anhydride (PA) + Glycerine $G(OH)_3$ ⟶



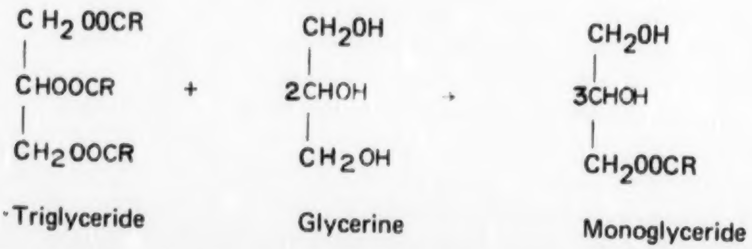
This will then react with the long chain oil monoglyceride or fatty acid (FA) to yield:



$$HOOC-PA-\underset{\substack{|\\ O\\ H}}{G}-PA-\underset{\substack{|\\ F\\ A}}{G}-PA-\underset{\substack{|\\ O\\ H}}{G}-PA-\underset{\substack{|\\ O\\ H}}{G}-PA-\underset{\substack{|\\ F\\ A}}{G}-PA-\underset{\substack{|\\ O\\ H}}{G}-OH$$

Short Oil Alkyd

Alkyds can be manufactured directly from a fatty acid, polyol and acid or from the fatty acid oil, polyol and acid. The second combination (oil, glycerine and PA) produces glyceryl phthalate which is insoluble in the oil and precipitates. This problem can be overcome by first converting the oil to a monoglyceride by heating with a polyol in the presence of a catalyst. This process is called alcoholysis of the oil. The basic reaction is shown below:



This is an ester interchange reaction with no loss of water.

When fatty acid rather than oil is used as the starting material, this is called the "one-stage" process. In this process, the fatty acid and glycerine are added to the kettle, the agitator is started and heat is introduced. When the batch reaches 440° F, the PA is slowly added and cooking continued for another 3 to 4 hours until the desired body and acid number are reached.

If the fusion process is being used, a continuous purge of inert gas is maintained to remove the water formed in the reaction. This water may also be removed by what is known as the solvent process. It is similar to the fusion process except that about 10% aromatic solvent (usually xylene) is added at the start. The vaporized solvent is passed into a condenser. The condensate then flows to a decant receiver for separation of reaction water. Recovered solvent is returned to the reactor.

As discussed earlier, when oil is used rather than fatty acid, the alkyds are produced in a two stage process. In the first stage the monoglyceride is first produced from the linseed oil and glycerol. Catalyst and oil are added and the alcoholysis of the polyol and oil is carried out between 450 and 500° F until the desired end point is reached. When the alcoholysis is completed, any additional polyol needed is added.

Following this, the required amount of PA and esterification catalyst are slowly added. If solvent cooking is to be used, the solvent is also added at this time. Cooking then proceeds as before.

A typical manufacturing formula for a 50% oil-modified glyceryl phthalate alkyd using the two stage process is given below.[4]

	lb
First stage	
Linseed oil	51.3
Glycerol (95%)	12.8
Catalyst, $Ca(OH)_2$	0.026
Second stage	
Glycerol (95%)	6.2
Phthalic Anhydride	39.7
Catalyst	
Methyl p-Toluene Sulfonate	0.2
	110.2
Approx. Loss	10.2
Solids Yield	100.0

Alkyd and other resins are cooked in closed set kettles, more properly called reactors. They vary in size in commercial production from 500 to 10,000 gallons. A typical reactor system is shown in Figure 4. They are generally fabricated of Type 304 or 316 stainless steel with well polished surfaces to assure easy cleaning. Design pressure is usually 50 psig. These reactors may be heated electrically, direct fired with gas or oil or indirectly heated using a heat transfer media such as Dowtherm(R). They are also equipped with a manway, sight-glass, charging and sampling line, condenser system, weigh tanks, temperature measuring devices and agitator. The manway is used both for charging solid material and for access to the kettle for cleaning and repair.

The reactor may be equipped with a variety of different condenser systems. The system shown in Figure 4 includes a packed fractionating column, a reflux condenser and a main condenser. The condensers are water cooled shell and tube type and may be either horizontally or vertically inclined. Vapors are processed and condensed on the tube side and drain to a decant receiver for separation and possible return of solvent to the reactor. A dual function aspirator Venturi scrubber is often added to the system. It is used to ventilate the kettle during addition of solid materials and may also remove entrained unreacted or vaporized solids and liquids from the venting gases.

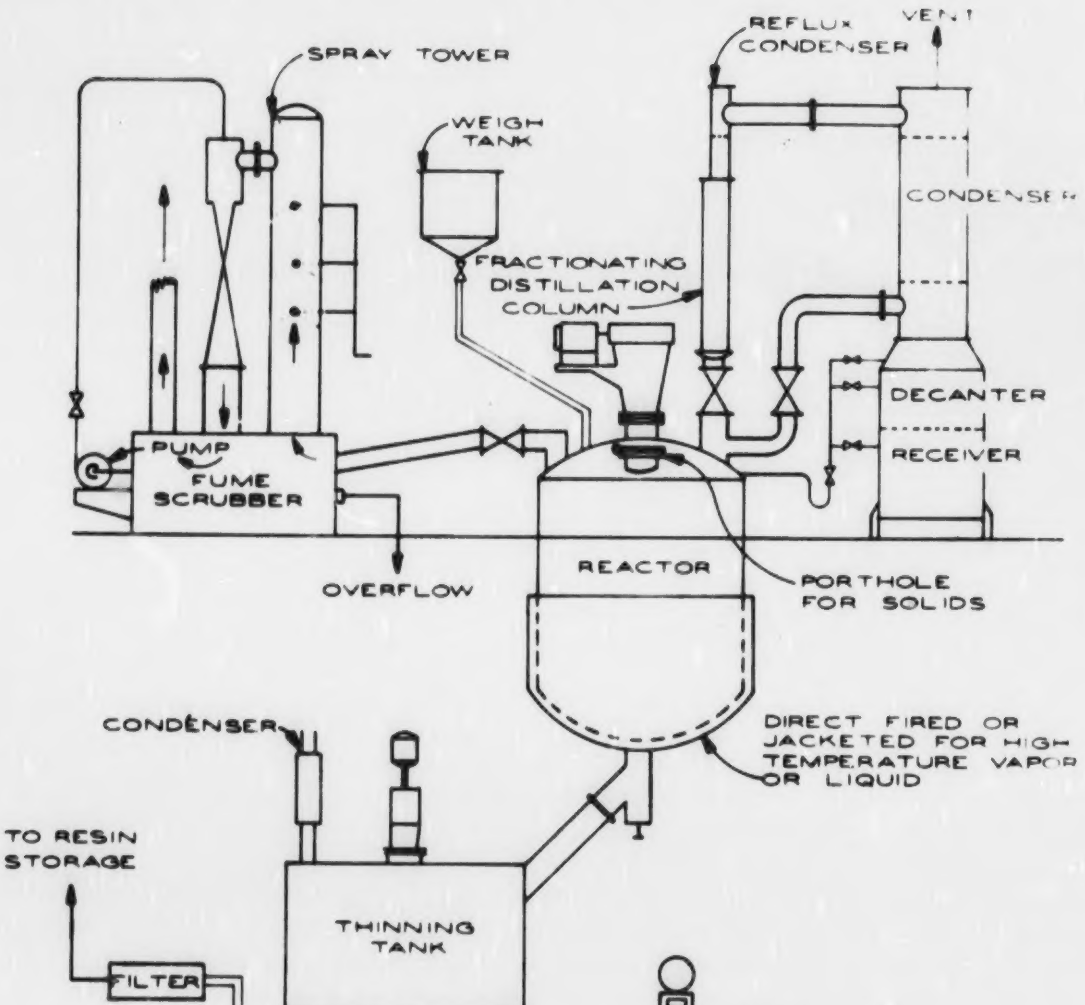


FIGURE 4
MODERN RESIN PRODUCTION SYSTEM
OF
SOLVENT AND FUSION COOKS

Thinning tanks are always included as part of the reactor system. They are normally water cooled and equipped with a condenser and agitator. The partially cooled finished alkyd is transferred from the reactor to the partially filled thinning tank. Since most alkyd resins are thinned to 50% solids, the capacities of these tanks are normally twice the capacity of the reactors. These tanks are also frequently mounted on scales so that thinning solvents may be accurately added.

The final step in a reactor system is filtering of the thinned resin prior to final storage. This is normally done while it is still hot. Filter presses are the most commonly used filtering device.

The manufacturing procedures and equipment used for the production of other resins listed at the beginning of this discussion are quite similar. The major differences are the raw materials and the process steps utilized. A detailed discussion of these other resins is beyond the scope of this narrative.

NATURE OF GASEOUS DISCHARGE

There are two major types of emissions from a paint plant. These are non-fugitive and fugitive. Non-fugitive emissions are those that are collected by and confined within an exhaust system. Fugitive emissions are those that escape into the plant atmosphere from various operations and exit the plant building through the doors and windows in an unregulated fashion.

In today's typical paint plant there are two types of fugitive emissions. These are pigment particulate and paint solvents. In a small percentage of the plants an attempt is made to collect these emissions. The incentive for doing so is based on insurance requirements as well as occupational health and safety rather than air pollution considerations or regulations. The newly passed OSHA regulations will have a dramatic effect on the paint industry practice and necessitate the regulation of fugitive emissions.

PARTICULATE CONTAMINANTS

Fugitive particulate emissions consist primarily of the various pigments used. As a general rule, the pigments are received and stored in 25 to 50 pound paper sacks or fiber drums. Modern pigment manufacturing has developed fine sized pigment, 0.05 to 0.25 microns, for ease of dispersion into the paint vehicle. Loading of these fine pigments into grinding equipment results in fugitive particulate dust emissions into the surrounding plant areas. This dust is either collected by a ventilation and exhaust system or allowed to settle and later collected as part of the general housekeeping requirements.

A variety of resins are received as granular or flaked solids which are of large size and do not result in a fugitive dust emission. The manufacturer of these solid resins, however, does encounter fugitive emission problems in his flaking or grinding operations.

GASEOUS CONTAMINANTS

Solvent emissions occur in almost every phase of paint and varnish manufacturing and in numerous locations throughout individual plants. A listing of emission points is given below.

	Location	Operation	Temp., °F	Pressure
1.	Resin Plant	Thinning	200 to 300° F	Atmospheric
2.	Resin Plant	Filtering	200 to 300° F	Atmospheric
3.	Resin Plant	Storage Tanks	100° F	Atmospheric
4.	Paint Plant	Blending Tanks	Ambient	Atmospheric
5.	Paint Plant	Milling	Ambient	Atmospheric
6.	Paint Plant	Dispersion	Ambient	Atmospheric
7.	Paint Plant	Holding Tank	Ambient	Atmospheric
8.	Paint Plant	Filtering	Ambient	Atmospheric

The extent of these emissions vary with the type of operation and the effort extended to control atmospheric losses. The high temperature thinning and filtering results in the largest emissions while packaging in drums and cans contribute the smallest emission. Other operations contribute intermediate emissions which vary depending on the degree of control exercised and the vapor pressure of the solvent used.

In some cases, efforts are made to collect fugitive emissions by use of ventilation hoods and a closed exhaust system. More frequently, however, they are exhausted from the building by general building exhaust fans which ventilate areas having the highest contaminant concentration.

Resin plants or paint plants producing resins and varnishes are likely to have a number of regulated emissions. These emissions consist primarily of gaseous hydrocarbons in air or inert gas streams. The three major sources of these regulated emissions are:

1. Varnish cooking
2. Resin cooking
3. Thinning

Other less concentrated streams that may or may not be regulated are:

1. Storage and rundown tank vent systems
2. Filter press vent systems
3. Sandmill vent systems

Considerable effort has been expended to identify the various types of chemical compounds emitted during a varnish cook. The majority of this work was done in the 1950's and is well summarized by R. L. Stenburg(3) in the H.E.W. Technical Report A58-4. A copy of his summary is included here as Table 2. In general, one or more of the following compounds are emitted, depending upon the ingredients in the cook and the cooking temperature; water vapor, fatty acids, glycerine, acrolein, phenols, aldehydes, ketones, terpene oils and terpene. These materials are mainly decomposition products of the varnish ingredients.

Varnishes and oils are cooked or bodied at temperatures from 200 to 650°F. At about 350°F decomposition begins and continues throughout the cooking cycle which normally runs between 8 and 12 hours. The quantity, composition and rate of emissions depends upon the ingredients in the cook as well as the maximum temperature, the length, the method of introducing additive, the degree of stirring and the use of inert gas blowing. In general, the emissions will average between one to three percent of the charge in oil bodying and three to six percent in varnish cooking. Aside from academic interest, the exact chemical structure of these emissions is not too important. Of more importance are the characteristics of the emissions related to ease of removal by the applicable pollution control devices.

Modern resin reactors and varnish cookers account for the majority of clear coatings production in the paint and varnish industry. As described earlier, these products are cooked in larger more carefully controlled reactors equipped with product recovery devices which also help reduce atmospheric emission.

As with the old varnish kettles, the amount of emissions vary with the type of cook, the cooking time, the maximum temperature, the initial ingredients as well as the type and method of introducing ingredients.

For solvent cooking the quantity of emission does not vary significantly with the size of the reactor but is rather more a function of the volatility of the solvent being used and the size and/or efficiency of the condenser. Since there is no sparge gas used in solvent cooking, exhaust volumes are small and consist primarily of noncondensed solvent fumes. Emissions will run from 0.1 to 0.5 pounds per hour and will be less cyclic in nature than for fusion cooks.

Emissions during fusion cooking run much higher and vary with the size of the reactor. The total exhaust volume is dependent primarily on the sparge rate of inert gas. Dean H. Parker(4) indicated typical sparge rates of 0.04 ft^3/min/gal of charge during the first hour, 0.02 ft^3 during the second, and 0.01 ft^3 during the remainder of the cook. The exhaust rate will average from 2 ft^3/min/100 gallons of capacity on small reactors to 1 ft^3/min/100 gallons of capacity on large reactors. A summary of source test results from a variety of resin reactors is presented in Table 3.(11)

Since fusion cooking is a cyclic batch process, the concentration of emission will vary from the start to finish of the cook. Hydrocarbon concentration will vary from 15,000 to 80,000 ppm as methane equivalent, depending on the time of the cycle and the type of cook. There are at least 100 different emission curves that could be encountered if one tried to cover all of the different cooking formulas. Particulate phthalic anhydride (PA) is also emitted from the kettle and concentration levels vary depending on cycle time, types of cook, method of charging and type of PA used. Charging of liquid PA rather than dry solid PA significantly reduces the

TABLE 2

COMPOSITION OF OIL AND VARNISH FUMES(3)

Bodying Oils	Running Natural Gums	Manufacturing Oleoresinous Varnish	Manufacturing Alkyd Varnish
Water vapor	Water vapor	Water vapor	Water vapor
Fatty acids	Fatty acids	Fatty acids	Fatty acids
Glycerine	Terpenes	Glycerine	Glycerine
Acrolein	Terpene Oils	Acrolein	Phthalic anhydride
Aldehydes	Tar	Phenols	Carbon dioxide
Ketones		Aldehydes	
Carbon dioxide		Ketones	
		Terpene Oils	
		Terpenes	
		Carbon dioxide	

TABLE 3

EMISSION DATA SUMMARY [11]

Resin Type	Reactor Size (gal)	EMISSION: RANGE (lb/hr)	EMISSION: AVERAGE (lb/hr)	Major Component	Average Reaction Temp. (°F.)	
Alkyds	4,000	0.07-1.45	0.7	Xylene	410-460	Solvent cook, based upon 4 resins.
	1,000	0.17-0.75	0.3	Xylene		Solvent/fusion cook, based upon 7 resins.
	1,000	0.44-1.74	1.0	Xylene		Solvent cook, based upon 4 resins.
						Emissions exceeded 8 pounds/hour during second stage charging.
Polyester	4,000	1.32-27.3	12.9	Propylene Glycol	400-410	Fusion cook, based upon 4 resins.
						Emissions exceeded 8 pounds/hour during charging, exotherm and sparging.
	1,000	0.35-2.23	1.18	Propylene Glycol		Fusion cook, based upon 8 resins.
Acrylics, Melamines	4,000	0.06-0.21	0.10	Butanol	220-250	Solvent cook, based upon 11 resins.
	1,000	0.15-0.16	0.15	Butanol		Solvent cook, based upon 2 resins.

emission rate. However, if the linear velocity of the sparge gas is maintained below 150 ft/min, the carryover of PA is also significantly reduced. Entrained and sublimed PA will run between 1 to 3 pounds per hour over a period of 50 to 70 minutes during and following the charging period. Plots of hydrocarbon emission level vs. time for three of many possible cooks are given as Figures 5, 6 and 7.(10) These emission concentrations are those measured directly out of a closed kettle or reactor.

Figure 7 shows typical variations in emissions from one batch to another when cooking the same product in the same kettle. Variations twice as great as this are not uncommon. Emissions increase dramatically and rapidly as indicated on Figures 5 and 6 whenever the loading hatches are opened. This is a result of forced exhaust of the kettle to prevent spillage of fumes into the room from the open hatch.

The storage of liquid PA will result in significant vaporization losses from the storage tank and an effort must be made to control these losses. The most widely used method consists of an inert gas blanketing in conjunction with a pressure controlled unit. The tank is also equipped with a water cooled condenser used to vent the tank during filling. After filling the condenser is then heated with steam to remove collected PA by melting.

POLLUTION CONTROL CONSIDERATIONS

Collection of particulate pigment or resin emission is a simple straightforward job. The only practical control device is a fabric filter, and it is ideally suited for this application. Collection efficiency for the submicron pigment dust (0.05 to 0.25 microns) is in the range of 99.9%. There are no temperature problems since the exhaust system runs at ambient temperatures. The grain loading is very low and baglife is extensive. Approximately 0.01% of the loaded pigments are lost and collected. Grain loadings to the fabric filter run around 0.19 grain/SCF. A typical collection system is shown in Figure 8. The collection system can be a fixed hood which can handle both dust and pigment bags or a flexible hose positioned above the loading hatch or attached to the top of the tank. The tank attachment provides the most positive control of fugitive dust emission but also increases pigment and solvent losses slightly.

The application of control equipment to this problem is quite simple and can be solved with standard off-the-shelf equipment from a host of suppliers. For this reason, detailed equipment cost and installation bids will not be required.

The control of hydrocarbon and odors from the various emission sources listed earlier is not quite as straightforward as the dust emission. There are three types of control equipment that have been applied to this problem. They are catalytic and thermal combustion devices, and wet scrubbers.

As a general rule, wet scrubbing does not provide a satisfactory solution for the following reasons:

FIGURE 5
HYDROCARBON EMISSION FOR DOWTHERM KETTLE

VAPOR TEMPERATURE RANGED FROM 100°F TO 340°F
KETTLE TEMPERATURE FROM 80°F TO 500°F
COOK RAN 20 HOURS

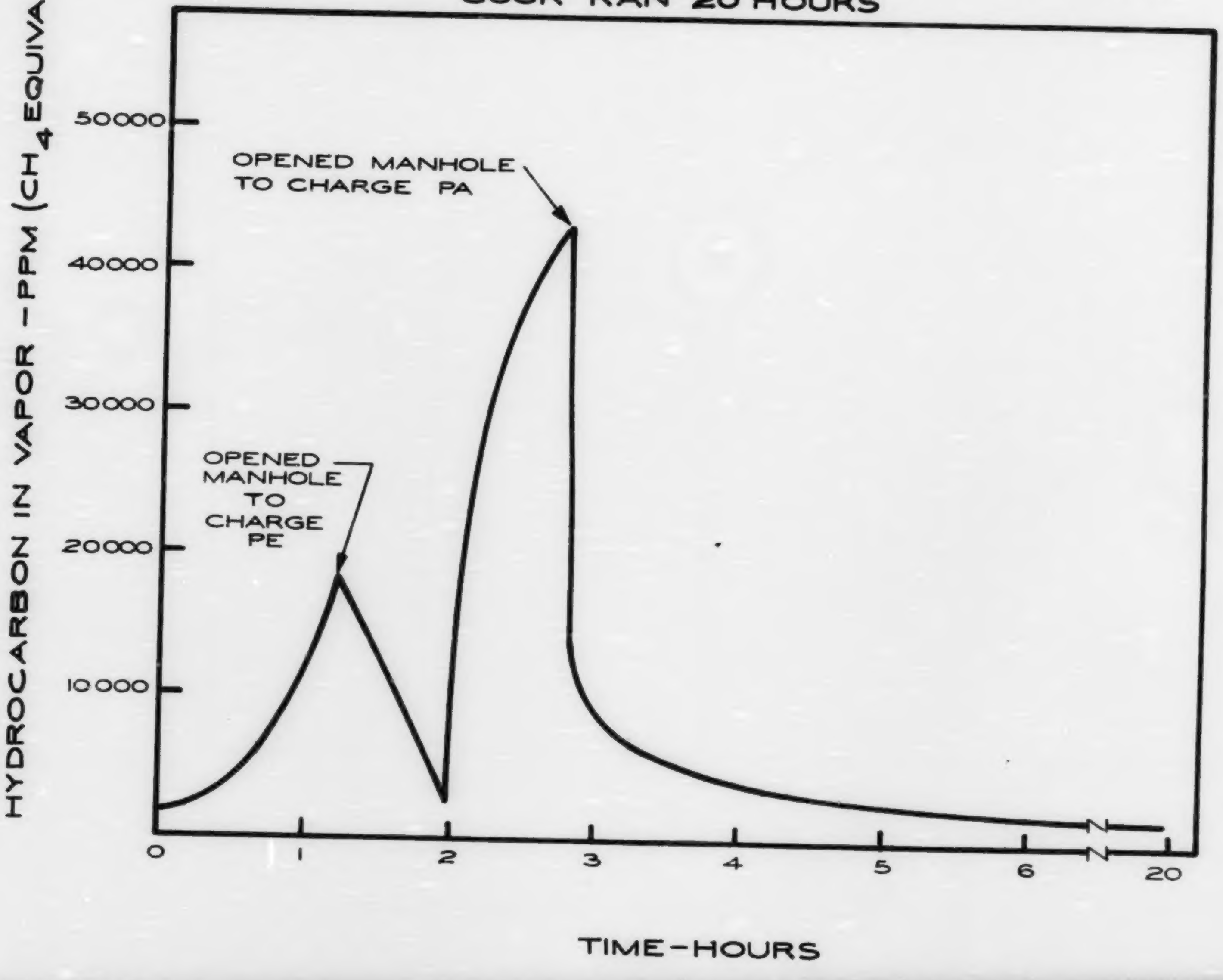


FIGURE 6

HYDROCARBON EMISSION FOR PAINT KETTLE

VAPOR TEMPERATURE RANGED FROM 100°F TO 310°F
KETTLE TEMPERATURE FROM 80°F TO 480°F

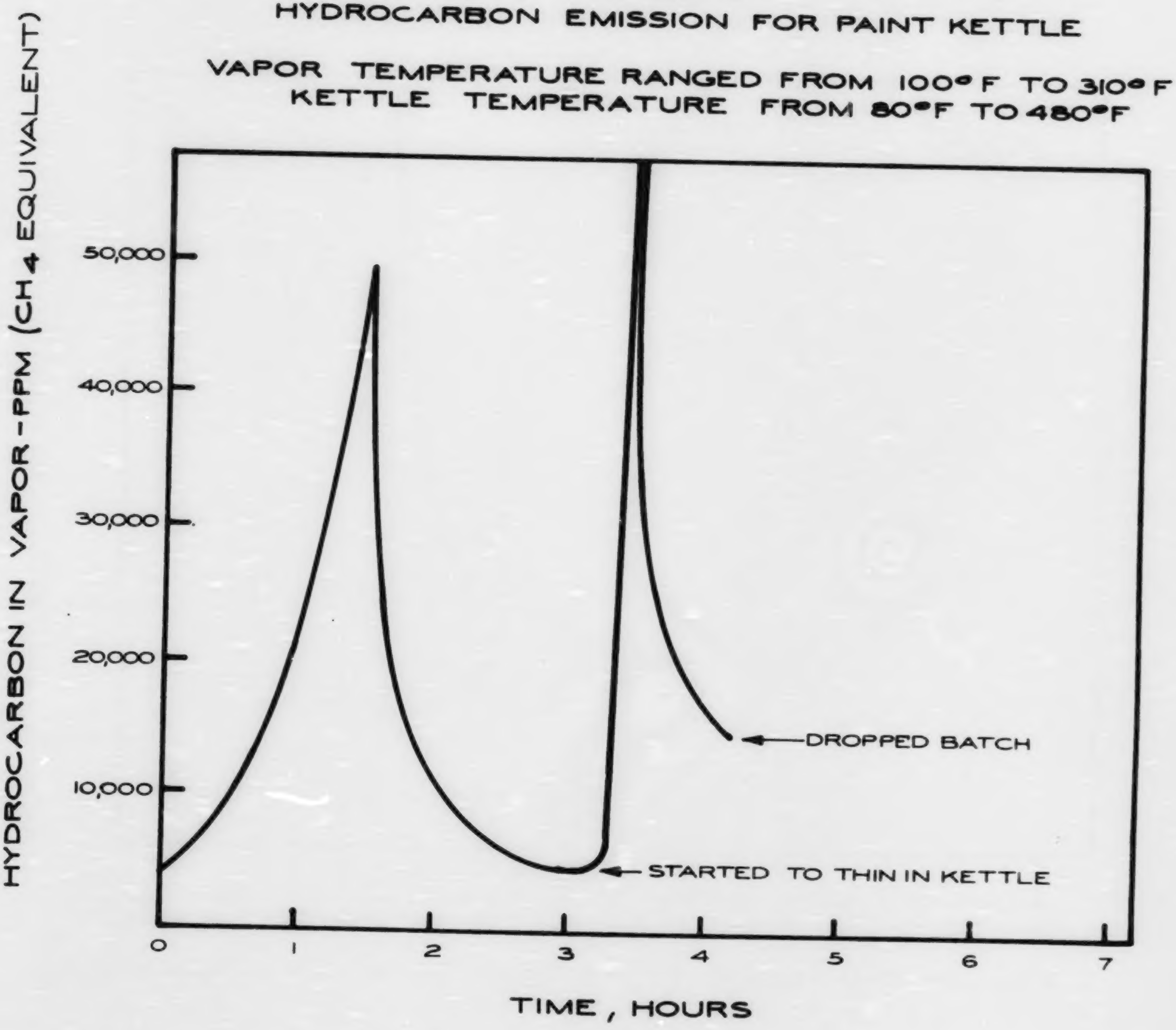


FIGURE 7
KETTLE HYDROCARBON EMISSON - 2 BATCHES MONITORED

VAPOR TEMPERATURE RANGED FROM 100°F TO 310°F
KETTLE TEMPERATURE RANGED UP TO 490°F

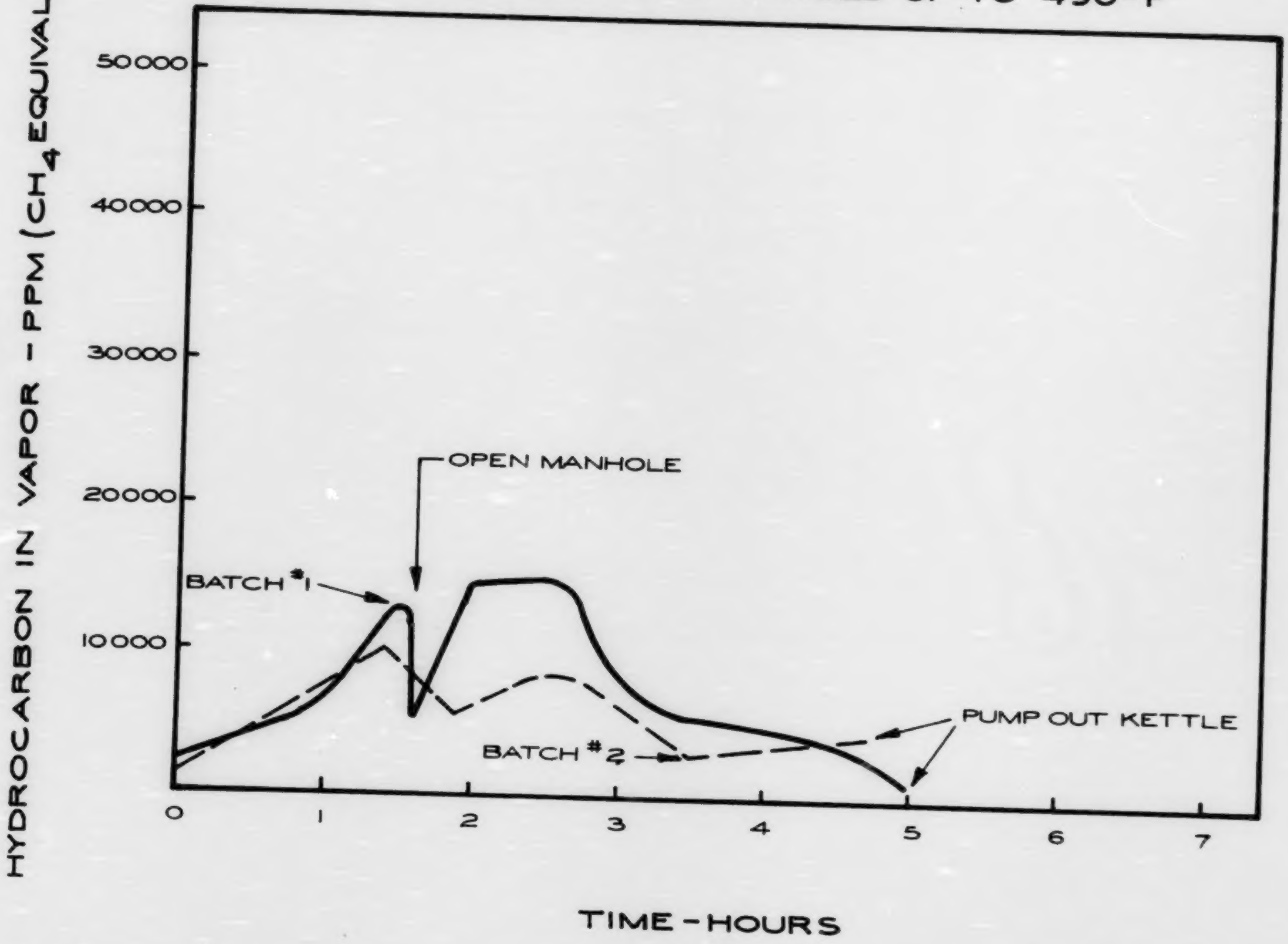
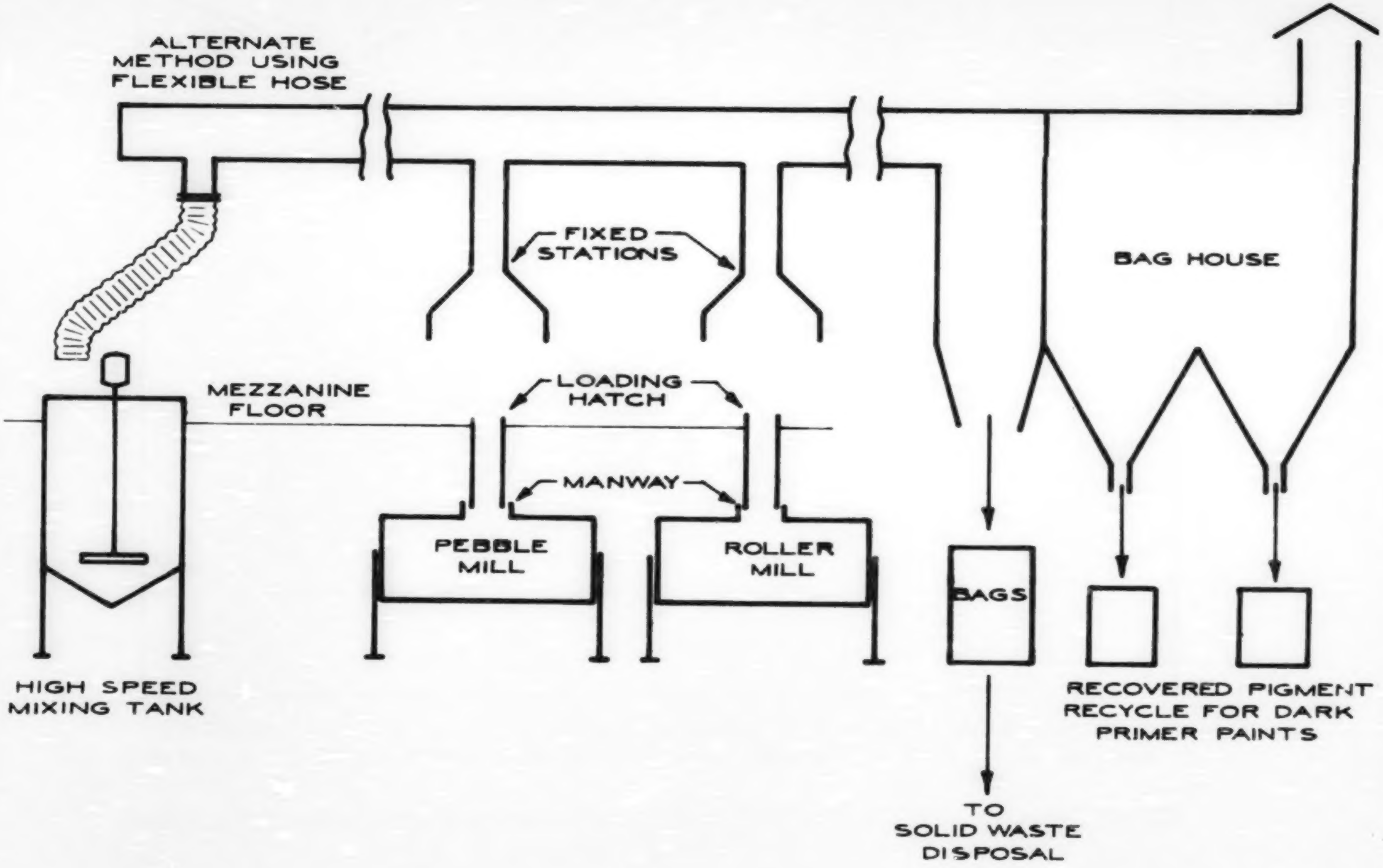


FIGURE 8

PIGMENT EMISSION CONTROL SYSTEM



1. Removal efficiency of fine hydrocarbon aerosol is not good at economically practical pressure drops.

2. Noncondensible hydrocarbon solvent vapors will not be removed.

3. Odor removal without the addition of an oxidizing agent such as potassium permanganate or sodium hypochorite is unsatisfactory. If an oxidizing agent is used, operating cost will be quite high due to the high concentration of other oxidizable material such as phthalic anydride, resins and oil.

4. Mobile packing and high make-up water rates are required to prevent plugging of the scrubber beds and spray nozzles.

5. Correction of the air pollution problem with wet scrubbing causes an equivalent water pollution problem which in many areas is more costly to correct than the original air pollution problem.

The only control technique currently being used that has proven effective for all cases is combustion. Three general methods are employed to combust waste gases, as shown below.

1. Flame Combustion
2. Thermal Combustion
3. Catalytic Combustion

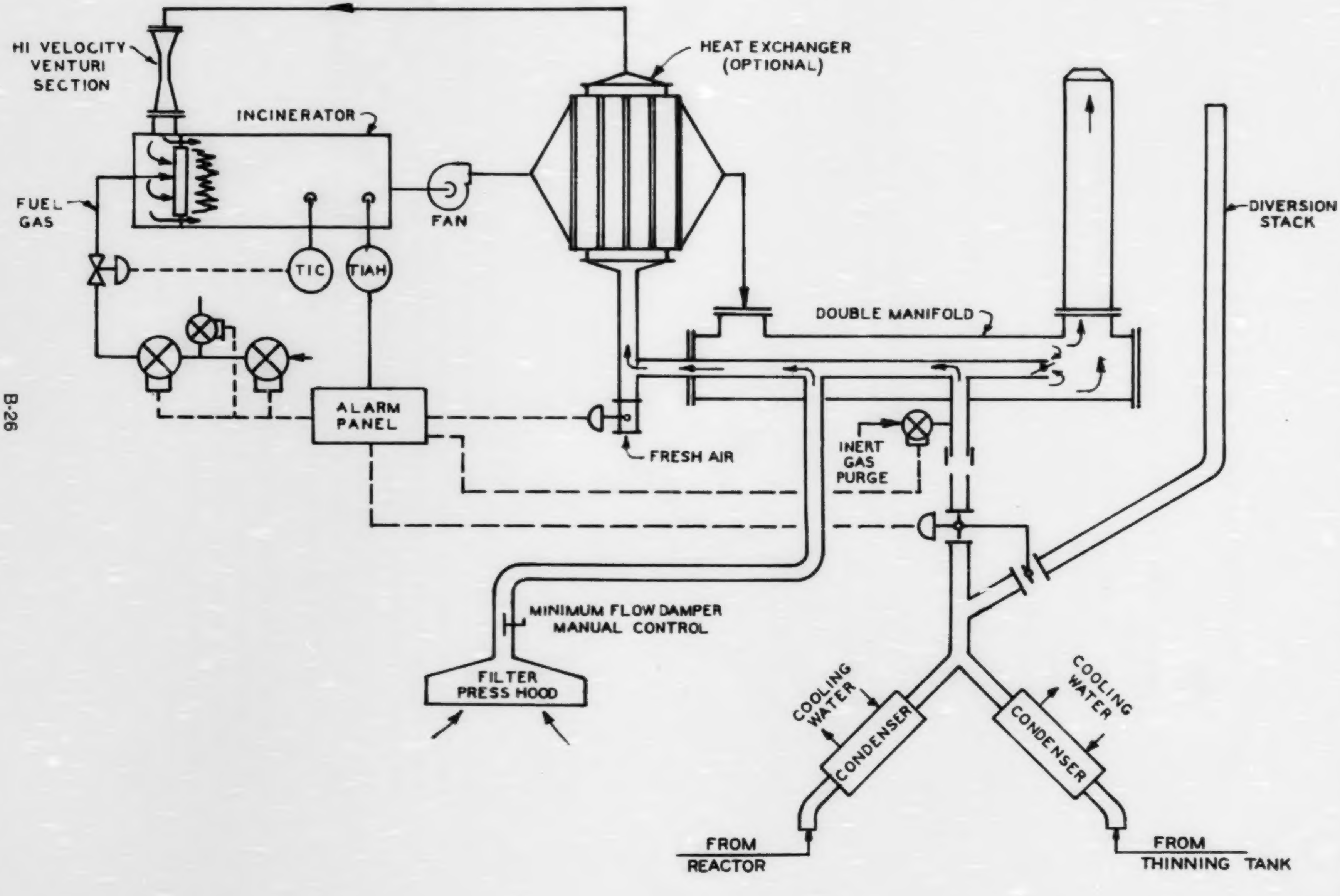
All of the above methods are oxidation processes. Ordinarily, each requires that the gaseous effluents be heated to the point where oxidation of the combustible will take place. The three methods differ basically in the temperature to which the gas stream must be heated.

Flame combustion is the easiest of the three to understand, as it comes the closest to everyday experience. When a gas stream is contaminated with combustibles at a concentration approaching the lower flammable limit, it is frequently practical to add a small amount of natural gas as an auxiliary fuel and sufficient air for combustion when necessary, and then pass the resulting mixture through a burner. The contaminants in the mixture serve as a part of the fuel. Flame incinerators of this type are most often used for closed chemical reactors. They are not used on resin reactors at present. They may be an ideal solution some day, however, when methods of operating a closed, pressurized resin reactor are developed.

It is far more likely that the concentration of combustible contaminants in an air stream will be well below the lower limit of flammability. When this is the case, direct thermal combustion is considerably more economical than flame combustion. Direct thermal combustion is carried out by equipment such as that illustrated in Figure 9. In this equipment, a gas burner is used to raise the temperature of the flowing stream sufficiently to cause a slow thermal reaction to occur in a residence chamber.

FIGURE 9

THERMAL AFTERBURNER SYSTEM
FOR
RESIN REACTOR OR CLOSED KETTLE



Whereas flame temperatures bring about oxidation by free radical mechanisms at temperatures of 2500° F and higher, thermal combustion of ordinary hydrocarbon compounds begins to take place at temperatures as low as 900 to 1000° F. Good conversion efficiencies are produced at temperatures in the order of 1400° F with a residence time of 0.3 to 0.6 seconds.

Catalytic combustion is carried out by bringing the gas stream into intimate contact with a bed of catalyst. In this system, the reaction takes place directly upon the surface of the catalyst, which is usually composed of precious metals, such as platinum and palladium. While thermal combustion equipment brings about oxidation at concentrations below the limits of flame combustion, catalytic combustion operated below the limits of flammability and below the normal oxidation temperatures of the contaminants. The reaction is instantaneous by comparison to thermal combustion and no residence chamber is required. Catalytic combustion is carried out by equipment such as that illustrated in Figure 10.

In general, catalytic afterburners are less expensive to operate, however, they depend directly on the performance of the catalyst for their effectiveness. It will not function properly if the catalyst become deactivated. Because of this, catalytic units are not inherently functional when operated at design conditions. In many areas, means for ensuring adequate performance of the catalyst on a long-term basis will be required by environmental control offices.

The basis for design of either catalytic or thermal combustion is the hydrocarbon concentration of the exhaust gases handled by the incinerator. The maximum hydrocarbon level is set by most insurance companies at one-quarter of the lower explosive limit (L.E.L.) which is equivalent to 13 BTU/SCF of exhaust gas. As outlined earlier, the quantity of emission may vary significantly with cooking time and the type of cook. There is also likely to be a large variety of different hydrocarbons emitted. For this reason, theoretical calculations of emissions for design purposes are not satisfactory. On site emission measurements, as shown earlier on Figures 5 and 6, are required. Once the rate of emission is determined, it is then necessary to calculate the dilution air required to meet 1/4 LEL and set up the duct work system to provide for this dilution. When possible, dilution air should be utilized to help capture as many fugitive fume emissions as possible. For example this can be accomplished by taking the dilution air from a hood positioned over the resin filter press and venting the thinning tanks and product rundown tanks into the same system.

A concentration of 1/4 LEL or 13 BTU/SCF will give a temperature rise of about 600° F in the afterburner. This is too high if a heat exchanger is to be used, and in these cases, we will dilute to a maximum concentration of 12 BTU/SCF. In all cases, the heat exchangers will be the parallel flow type having a thermal efficiency of 42%. This is required due to the high emission concentration to assure temperature balance and control.

The major problem with catalytic or thermal afterburners as applied to open or closed resin and varnish kettles is the danger of fires and/or explosions. This has happened in numerous occasions in the past due primarily to excessive hydrocarbon emission from kettles. These problems have been all but eliminated on newer units by assuring that the design was based on actual emission measurements of the highest emitting cook and the addition of some of the

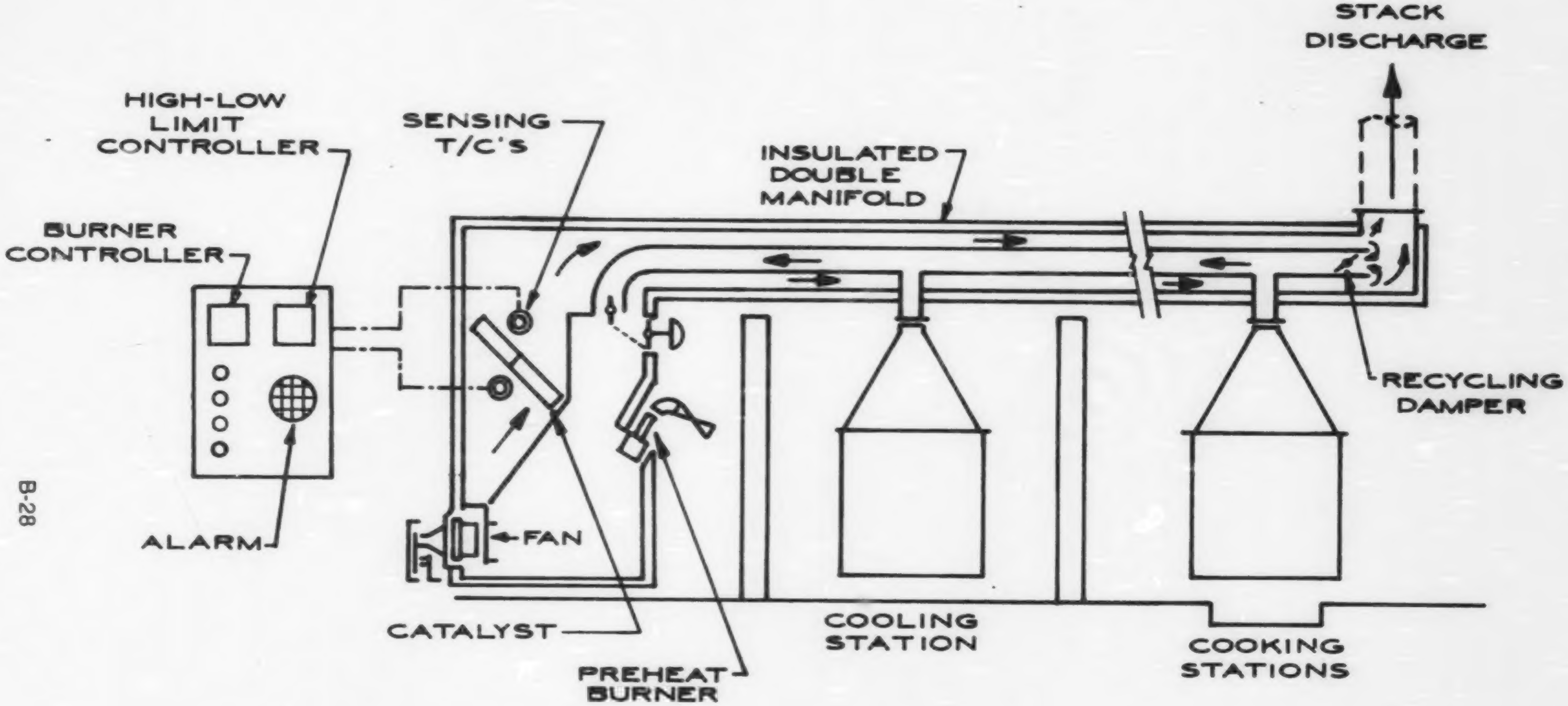


FIGURE 10

SCHEMATIC DIAGRAM OF A CATALYTIC INCINERATION SYSTEM FOR VARNISH KETTLES following system safety features:

1. High limit temperature alarm to shut off burner and activate a diversion system.
2. High velocity duct section to assure gas flow to afterburner substantially exceeds flame propogation velocity of hydrocarbons being burned.
3. Double manifolding or hot gas recycle to prevent condensation of heavy hydrocarbons or phthalic anhydride.
4. Diversion system to block off hydrocarbon emissions to unit, by-passing them directly out of separate exhaust and introduce fresh air to purge the unit.
5. Pneumatic operation of the diversion system to assure fast positive action and provide a fail-safe system in the event of either air or electrical failure.
6. Purging with inert gas in the event of power failure.

The above general requirements are applicable to all types of afterburner control. Specific details for each type of system will be given in the equipment specifications.

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APPENDIX C-1

CAPITAL AND OPERATING COST FORMS

APPENDIX C

ESTIMATED CAPITAL COST DATA
(COSTS IN DOLLARS)

	LA Process Wt.		High Efficiency	
	Small	Large	Small	Large
Effluent Gas Flow				
ACFM				
°F				
SCFM				
Moisture Content, Vol. %				
Effluent Contaminant Loading				
gr/ACF (ppm)				
lb/hr				
Cleaned Gas Flow				
ACFM				
°F				
SCFM				
Moisture Content, Vol. %				
Cleaned Gas Contaminant Loading				
gr/ACF (ppm)				
lb/hr				
Cleaning Efficiency, %				
(1) Gas Cleaning Device Cost				
(2) Auxiliaries Cost				
(a) Fan(s)				
(b) Pump(s)				
(c) Damper(s)				
(d) Conditioning, Equipment				
(e) Dust Disposal Equipment				
(3) Installation Cost				
(a) Engineering				
(b) Foundations & Support				
Ductwork				
Stack				
Electrical				
Piping				
Insulation				
Painting				
Supervision				
Startup				
Performance Test				
Other				
(4) Total Cost				

APPENDIX C

ANNUAL OPERATING COST DATA
(COSTS IN $/YEAR)

Operating Cost Item	Unit Cost	Thermal		Catalytic	
		Small	Large	Small	Large
Operating Factor, Hr/Year					
Operating Labor (if any)					
Operator	$6.00				
Supervisor	$8.00				
Total Operating Labor					
Maintenance					
Labor	$6.00				
Materials (Average)		145	195	105	135
Total Maintenance					
Replacement Parts (Average)		370	440	1200	4000
Total Replacement Parts					
Utilities					
Electric Power	$0.011				
Fuel	$0.80				
Water (Process)	$0.25				
Water (Cooling)	$0.05				
Chemicals, Specify					
Total Utilities					
Total Direct Cost					
Annualized Capital Charges					
Total Annual Cost					

APPENDIX D-1

EPA SOURCE TEST DATA

TABLE D-1 MASS EMISSIONS AND PROCESS DATA

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in. of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (^oF)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/9-10/73 - ALKYD FUSION COOK - KETTLE #4 - RUN #2									
	Load Soya & Linseed Oil								
1435-1526	Heat to 300°F	840		0		80			
1526-1530	Add PE*	800	0.240			145	470.94	0.7044	3.0730
1530-1805	(Heat to 350°F) (Add Catalyst) (Heat to 440°F)	881	0.032	5		84	181.29	0.2986	1.3027
1805-1835	Hold for Clear	952	0.002	5		82	38.59	0.0686	0.2994
1835-1915	Cool to 385°F	714		5		80			
1915-1923	Add Phthalic Anhydride	740	0.007	5		79	72.40	0.1001	0.4369
1923-2230	Heat to 460°F (some steam ejections)	605	0.023	5		86	153.44	0.1736	0.7572
2230-2320	Inert Gas 20 CFM	1012	0.110	20		118	325.19	0.6172	2.6927
2320-0120	Inert Gas 30 CFM	1294	0.044	29		107	208.29	0.5039	2.1986
0120-0150	(Cooling to Drop) (Drop)	740	0.002	10		110	37.64	0.0520	0.2270

*Pentaerythritol

TABLE D-2 MASS EMISSIONS AND PROCESS DATA

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in. of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (°F)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/10/73 - ALKYD FUSION COOK - KETTLE #4 - RUN #3									
	Load Soya & Linseed Oil								
0230-0342	Heat to 300°F	619	0.004	9.8		110	55.82	0.0645	0.2942
0342-0345	Add PE*	573	0.330			100	573.60	0.6145	2.8033
0345-0600	(Heat to 350°F) (Add Catalyst) (Heat to 440°F)	958	0	9.9		75			
0600-0630	Hold for Clear	794	0	9.9		74			
0630-0725	Cool to 360°F	435	0.003			74	49.97	0.0406	0.1851
0725-0728	Add Phthalic Anhydride	588	0	9.3		74			
0728-0900	Cool to 355°F (Boiler Out)	485	0			73			
0900-1150	Heat to 460°F	365	0	9.8		79			
1150-1250	Inert Gas 20 CFM	731	0.023	19.1		93	152.52	0.2084	0.9508
1250-1405	Inert Gas 30 CFM	898	0.029	28.8		94	171.11	0.2872	1.3105
1405-1554	(Cooling to Drop) (Drop)	357	0	5		107			

*Pentaerythritol

TABLE D-3 MASS EMISSIONS AND PROCESS DATA

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in. of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (°F)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/11/73 - ALKYD SOLVENT COOK - KETTLE #2 - RUN #1									
	Load Soya Acid Pentaerythritol, Crotonic Acid (Steam Ejector)								
0200-0415	Agitation, Heat to 300°F					70			
0415-0430	Add Phthalic Anhydride								
0430-0521	Start Condensor & Add Xylene	28102			1.286	63	1.10	.0010	.0017
0521-0820	Reflux & Heat to 350°F	37781				68			
0820-1545	Reflux & Heat	34230			0.426	76	0.36	.0004	.0007
1545-2000	Hold at 480°F	75366			0.221	89	0.18	.0004	.0008
	Dump								

TABLE D-4 MASS EMISSIONS AND PROCESS DATA

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in. of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (^oF)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/11-12/73 - POLYESTER RESIN COOK - KETTLE #8 - RUN #1									
2046-2245	Polyglycol Wash	37536			4.756	72	4.060	0.0047	0.0250
2246-0040	Loading (Steam Ejector)	5430	0.140			128	586.67	5.9560	31.5967
0040-0130	Heating Prior to Reflux				0.470	68	0.40		
0130-0434	Reflux, Heating to 400^oF (H_2O Removed)				0.170	67	0.15		
0434-0705	Reflux, No H_2O Removed	82514	0.108			73	37.45	5.7782	30.6537
0705-1341	Vacuum Cycles	38193	0.285			80	33.90	2.4210	12.8435
7/12-13/73 - POLYESTER RESIN COOK - KETTLE #8 - RUN #2									
1537-1750	Polyglycol Wash	16262	0.680	30		96	91.66	2.7868	15.4221
1750-1900	Loading (Steam Ejection)	5487	0.370			126	951.00	9.7561	53.9905
1900-2122	Heating Prior to Reflux	18157			0.624	85	0.51	0.0003	0.0016

TABLE D-4 MASS EMISSIONS AND PROCESS DATA (CONTIN.)

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in. of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (^oF)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
2122-0105	Reflux, Heating to 400^{o}F (H_2O Removed)	46553			0.118	81	0.10	0.0002	0.0008
0105-0303	Reflux, No H_2O being removed	86753	0.280	10		80	59.68	9.6802	53.5708
0303-0940	Vacuum Cycles	41644	0.030			80	10.99	0.8555	4.7345

TABLE D-5 MASS EMISSIONS AND PROCESS DATA

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in.of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (°F)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/16-17/73 - ALKYD FUSION COOK (SOYA) - KETTLE #3 - RUN #1									
1556-1615	Load Soya Oil	511	0.006	8		87	79.46	0.0759	0.3437
1615-1715	Heat to 400°F	1782	0.007	8		83	86.14	0.2870	1.2996
1715-1722	Add Pentaerythritol & NaOH (steam)	785	0.012			80	369.74	0.5426	2.4575
1722-1900	Heat to 450°F	785	0.007	7.9		80	86.39	0.1268	0.5740
1900-1915	Cool to 390°F	785	0.007	7.9		82	86.23	0.1265	0.5730
1915-2006	Add Phthalic Anhydride & Soya Oil (heating to 480°F)	876	0.006	7.8		81	79.92	0.1309	0.5927
2006-2305	Heat to 480°F	236	0.007	7.9		75	86.84	0.0382	0.1732
2305-0054	Inert Gas 10 CFM	673	0.004	9		75	65.69	0.0826	0.3740
0054-0111	Attempt 20 CFM Flow (Failed)	710	0.001			75	32.85	0.0435	0.1970
0111-0340	Cool Prior to Drop	501	0.003	9		75	59.93	0.0533	0.2415

TABLE D-6 MASS EMISSIONS AND PROCESS DATA

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in.of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (°F)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/17/73 - ALKYD FUSION COOK (SOYA) - KETTLE #3 - RUN #2									
0417-0426	Load Soya Oil	1247	0.006			80	80.16	0.1869	1.0482
0426-0607	Heat to 400°F	1812	0.002	12		82	46.19	0.1564	0.8774
0607-0616	Add Pentaerythritol & NaOH (steam)	965	0.092			73	345.29	0.6392	3.5847
0616-1000	Heat to 450°F	1026	0.003	12		75	56.96	0.1092	0.6124
1000-1030	Cool to 390°F	859	0.004	12		75	65.76	0.1055	0.5918
1030-1113	Add Phthalic Anhydride & Soya Oil	1151	0.005	5		80	73.18	0.1574	0.8829
1113-1345	Heat to 480°F	305	0.006	8		83	79.96	0.0455	0.2553
1345-1445	Inert Gas 10 CFM	496	0.008	9		85	92.16	0.0854	0.4791
1445-1600	Inert Gas 20 CFM	744	0.001	18.7		85	32.58	0.0452	0.2536
1600-1905	Cool Prior to Drop	299	0.009	14.3		82	98.02	0.0548	0.3070

TABLE D-7 MASS EMISSIONS AND PROCESS DATA

Time Interval	Process Mode	Avg. THC (ppm-C)	Avg. ΔP (in. of H_2O)	Avg. Inert Gas Flowmeter Reading (CFM)	Measured Flow Bag (ACFM)	Avg. Stack Temp. (°F)	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/18/73 - ALKYD SOLVENT COOK - KETTLE #2 - RUN #3									
0300-0344	Load Soya Acid	631	0.004	8		128	79.33	0.0936	0.1246
0344-0444	Pentaerythritol	431	0.865	23		110	1328.64	1.0706	1.4258
0444-0508	Crotonic Acid (Steam Ejector)	243	0.865	23		115	1322.86	0.6010	0.8003
0508-0710	Agitation, Heat to 300°F	1291	0.015	24		75	180.63	0.4360	0.5806
0710-0722	Add Phthalic Anhydride	2678	0.013	24.5		76	168.03	0.8413	1.1204
0722-0843	Start Condensor & Add Xylene	87908			0.172	80	0.15	0.0004	0.0005
0843-0930	Reflux & Heat to 350°F	40260			0.273	80	0.23	0.0003	0.0004
0930-1500	Reflux & Heat to 480°F	55326			0.314	87	0.27	0.0004	0.0006
1500-1545	Hold at 480°F	67970			0.359	91	0.30	0.0007	0.0009
1854	Dump								

TABLE D-8 THINNING TANK EMISSION DATA

Date	Time Interval	Tank No.	Solvent	Average ΔP (in. of H_2O)	Stack Temp. (°F)	Average THC (ppm-C)	Average Rate (SCFM)	Average THC Mass Emissions (#'s/hr.)
7/16/73	2150-2206	7	Mineral Spirits	-	75	37,362	-	-
7/17/73	0713-0729	6	Xylene	0.005	90	71,844	40.78	5.4783
7/17/73	1905-1911	3	Mineral Spirits	0.014	85	73,200	34.18	4.6778
7/18/73	0230-0244	2	Xylene	-	75	48,416	-	-
7/18/73	1428-1430	5	Mineral Spirits	0.051	90	100,650	64.90	12.2122
7/18/73	1615-1622	7		-	100	31,371	-	-
7/18/73	1639-1642	6	Mineral Spirits	0.014	100	36,666	75.82	5.1975
7/18/73	1845-1854	2	Xylene	1.460	100	99,343	344.11	63.9144

TABLE D-9 THINNING TANK EMISSION DATA SUMMARY

Date	Time Interval	Tank No.	Solvent	Flow Rate (SCFM)	THC #'s/hr	% n-Aliphatics (C_6-C_{10})	% Aromatics (C_6-C_8)	% Identified Oxygenates	% Branched Aliphatics (C_8-C_{12}) & Unknown Compounds
7-16-73	2[illegible]50-2206	7	Mineral Spirits			30.06	9.26	8.03	52.65
7-17-73	0713-0729	6	Xylene	40.78	5.4783		99		
7-17-73	1905-1911	3	Mineral Spirits	34.18	4.6778				
7-18-73	0230-0244	2	Xylene						
7-18-73	1428-1430	5	Mineral Spirits	64.90	12.2122				
7-18-73	1615-1622	7							
7-18-73	1639-1642	6	Mineral Spirits	75.82	5.1975	13.85	23.11	1.08	62.77
7-18-73	1845-1854	2	Xylene	344.11	63.9144		99		

TABLE D-10 MASS EMISSION DATA SUMMARY

Time Interval	Process Mode	% n-Aliphatics (C_6-C_{10})	% Aromatics (C_6-C_8)	% Identified Oxygenate	% Branched Aliphatics (C_8-C_{12}) & Unknowns	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/9-10/73 - ALKYD FUSION COOK - KETTLE #4 - RUN #2								
	Load Soya & Linseed Oil							
1435-1526	Heat to 300°F							
1526-1530	Add Pentaerythritol					470.94	0.7044	3.0730
1530-1805	(Heat to 350°F) (Add Catalyst) (Heat to 440°F)					181.29	0.2986	1.3027
1805-1835	Hold for Clear					38.59	0.0686	0.2994
1835-1915	Cool to 385°F		NO DATA AVAILABLE					
1915-1923	Add Phthalic Anhydride					72.40	0.1001	0.4369
1923-2230	Heat to 460°F (some steam ejections)					153.44	0.1736	0.7572
2230-2320	Inert Gas 20 CFM					326.19	0.6172	2.6927
2320-0120	Inert Gas ∿ 30 CFM					208.29	0.5039	2.1986
0120-0150	(Cooling to Drop) (Drop)					37.64	0.0520	0.2270

TABLE D-11 MASS EMISSION DATA SUMMARY

Time Interval	Process Mode	% n-Aliphatics (C_6- C_{10})	% Aromatics (C_6-C_8)	% Identified Oxygenates	% Branched Aliphatics (C_8- C_{12}) & Unknowns	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/18/73 - ALKYD SOLVENT COOK - KETTLE #2 - RUN #3								
0300-0344	Load Soya Acid					79.33	0.0936	0.1246
0344-0444	Pentaerythritol					1328.64	1.0706	1.4358
0444-0508	Crotonic Acid (Steam Ejector)					1322.86	0.6010	0.8003
0508-0710	Agitation, Heat to 300°F					180.63	0.4360	0.5806
0710-0722	Add Phthalic Anhydride					168.03	0.8413	1.1204
0722-0843	Start Condensor & Add Xylene		~99% After Xylene Addition			0.15	0.0004	0.0005
0843-0930	Reflux & Heat to 350°F					0.23	0.0003	0.0004
0930-1500	Reflux & Heat to 480°F					0.27	0.0004	0.0006
1500-1545	Hold at 480°F					0.30	0.0007	0.0009
1854	Dump							

TABLE D-12 MASS EMISSION DATA SUMMARY

Time Interval	Process Mode	% n-Aliphatics (C_6-C_{10})	% Aromatics (C_6-C_8)	% Identified Oxygenate	% Branched Aliphatics (C_8-C_{12}) & Unknowns	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/17/73 - ALKYD FUSION COOK (SOYA) - KETTLE #3 - RUN #2								
0417-0426	Load Soya Oil					80.16	0.1869	1.0482
0426-0607	Heat to 400°F					46.19	0.1564	0.8774
0607-0616	Add PE* & NaOH (steam)					354.29	0.6392	3.5847
0616-1000	Heat to 450°F					56.96	0.1092	0.6124
1000-1030	Cool to 390°F					65.76	0.1055	0.5918
1030-1113	Add Phthalic Anhydride & Soya Oil					73.18	0.1574	0.8829
1113-1345	Heat to 480°F					79.96	0.0455	0.2553
1345-1445	Inert Gas ∿ 10 CFM					92.16	0.0854	0.4791
1445-1600	Inert Gas 20 CFM	13.03%	14.3%	3.90%	68.70%	32.68	0.0452	0.2536
1600-1905	Cool Prior to Drop					98.02	0.0548	0.3070

*Pentaerythritol

TABLE D-13 MASS EMISSION DATA SUMMARY

Time Interval	Process Mode	% n-Aliphatics (C_6-C_{10})	% Aromatics (C_6-C_8)	% Identified Oxygenate	% Branched Aliphatics (C_8-C_{12}) & Unknowns	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/16-17/73 - ALKYD FUSION COOK (SOYA) - KETTLE #3 - RUN #1								
1556-1615	Load Soya Oil					79.46	0.0759	0.3437
1615-1715	Heat to 400°F					86.14	0.2870	1.2996
1715-1722	Add PE* & NaOH (steam)					369.74	0.5426	2.4575
1722-1900	Heat to 450°F					86.39	0.1268	0.5740
1900-1915	Cool to 390°F					86.23	0.1265	0.5730
1915-2006	Add Phthalic Anhydride & Soya Oil (Heating to 480°F)					79.92	0.1309	0.5927
2006-2305	Heat to 480°F	12.88	2.73	5.81	78.52	86.84	0.0382	0.1732
2305-0054	Inert Gas 10 CFM	6.04	5.98	8.51	79.46	65.69	0.0826	0.3740
0054-0111	Attempt ∿ 20 CFM Flow					32.85	0.0435	0.1970
0111-0340	Cool Prior to Drop					59.93	0.0533	0.2415

*Pentaerythritol

TABLE D-14 MASS EMISSION DATA SUMMARY

Time Interval	Process Mode	% Glycols	% Methanol	% Identified Oxygenates	Unknown Compounds	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/11-12/73 - POLYESTER RESIN COOK - KETTLE #8 - RUN #1								
2046-2245	Polyglycol Wash					4.060	0.0047	0.0250
2246-0040	Loading (Steam Ejector)					586.67	5.9560	31.5967
0040-0130	Heating Prior to Reflux			∿90% During Entire Process		0.40		
0130-0434	Reflux, Heating to 400°F (H_2O Removed)					0.15		
0434-0705	Reflux, No H_2O Removed	18.0%	82.0%			37.45	5.7783	30.6537
0705-1341	Vacuum Cycles					33.90	2.4210	12.8435
*	Vacuum at 10" of H_2O	90.0%			9.94%			
	Vacuum at 20" of H_2O	99%						

* These samples were not taken during this run but during similar modes of a non-monitored run.

TABLE D-14 MASS EMISSION DATA SUMMARY (CONTIN.)

Time Interval	Process Mode	% Glycols	% Methanol	% Identified Oxygenates	Unknown Compounds	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/12-13/73 - POLYESTER RESIN COOK - KETTLE #8 - RUN #2								
1537-1750	Polyglycol Wash					91.66	2.7868	15.4221
1750-1900	Loading (Steam Ejection)					951.00	9.7561	53.9905
1900-2122	Heating Prior to Reflux		NO DATE AVAILABLE			0.51	0.0003	0.0016
2122-0105	Reflux, Heating to 400°F (H_2O Removed)					0.10	0.0002	0.0008
0105-0303	Reflux, No H_2O being removed					59.68	9.6802	53.5708
0303-0940	Vacuum Cycles					10.99	0.8555	4.7345
	Drop							

TABLE D-15 MASS EMISSION DATA SUMMARY

Time Interval	Process Mode	% n-Aliphatics (C_6-C_{10})	% Aromatics (C_6-C_8)	% Identified Oxygenates	% Branched Aliphatics (C_8-C_{12}) & Unknown	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/11/73 - ALKYD SOLVENT COOK - KETTLE #2 - RUN #1								
	Load Soya Acid, Pentaerythritol, Crotonic Acid (Steam Ejector)							
0200-0415	Agitation, Heat to 300°F							
0415-0430	Add Phthalic Anhydride							
0430-0521	Start Condensor & Add Xylene		~99% After Xylene Addition			1.10	.0010	.0017
0521-0820	Reflux & Heat to 350°F							
0820-1545	Reflux & Heat to 480°F					0.36	.0004	.0007
1545-2000	Hold at 480°F					0.18	.0004	.0008
	Dump							

TABLE D-16 MASS EMISSION DATA SUMMARY

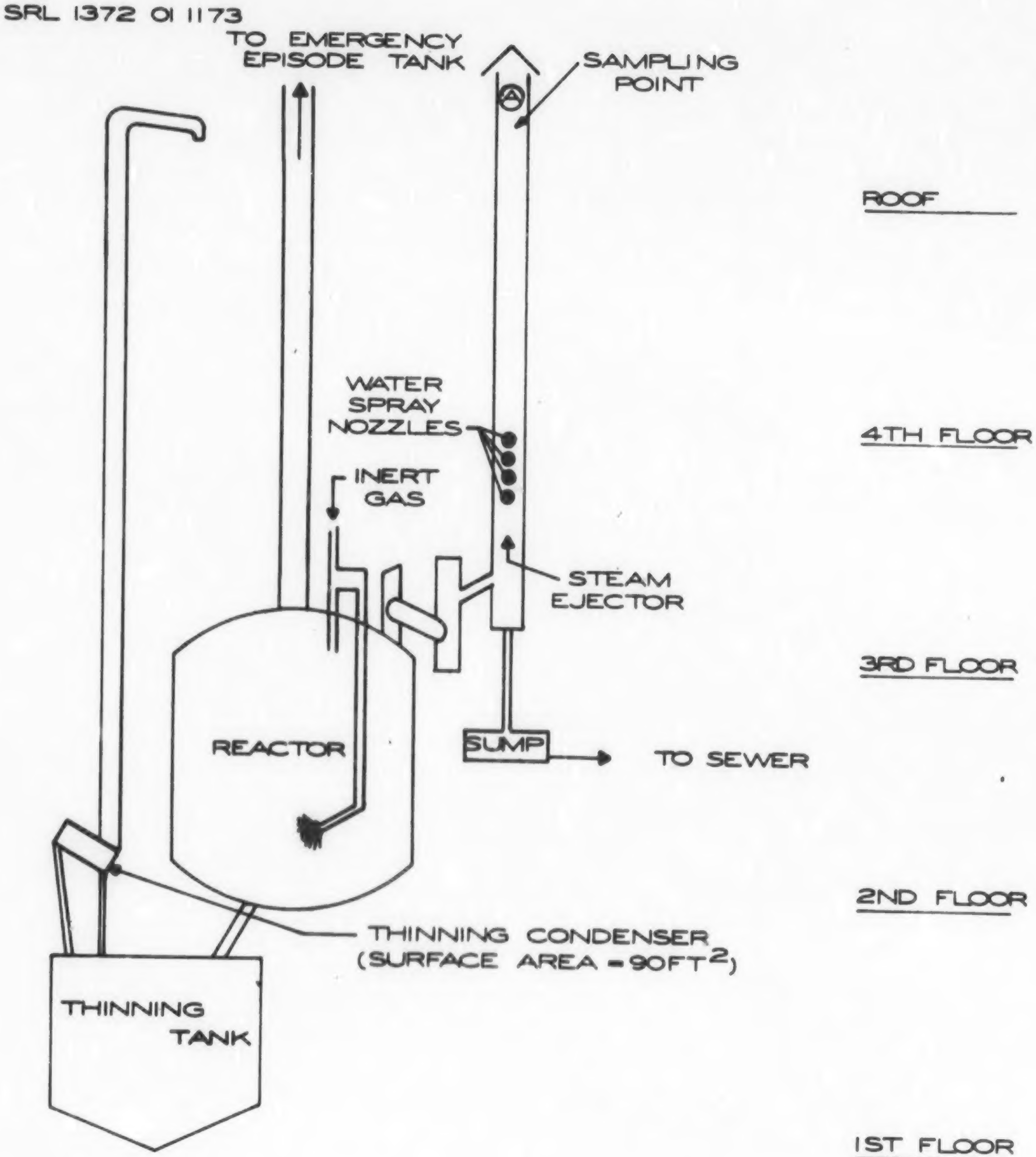
Time Interval	Process Mode	% n-Aliphatics (C_6-C_{10})	% Aromatics (C_6- C_8)	% Identified Oxygenate	% Branched Aliphatics (C_8- C_{12}) & Unknowns	Avg. Flow Rate (SCFM)	Avg. THC Mass Emissions (#'s/hr.)	T.H.C. Mass Emissions #'s/Ton of Resin Produced
7/10/73 - ALKYD FUSION COOK - KETTLE #4 - RUN #3								
	Load Soya Linseed Oil							
0230-0342	Heat to 300°F					55.82	0.0645	0.2942
0342-0345	Add Pentaerythritol					573.60	0.6145	2.8033
0345-0600	(Heat to 350°F) (Add Catalyst) (Heat to 440°F)	NO DATA AVAILABLE						
0600-0630	Hold for Clear							
0630-0725	Cool to 360°F					49.97	0.0406	0.1851
0725-0728	Add Phthalic Anhydride							
0728-0900	Cool to 355°F (Boiler Out)							
0900-1150	Heat to 460°F							
1150-1250	Inert Gas ∿20 CFM					152.52	0.2084	0.9508
1250-1405	Inert Gas ∿30 CFM					171.11	0.2872	1.3105
1405-1445	(Cooling to Drop) (Drop)							

TABLE D-17 THERMAL AFTERBURNER RAW DATA

Reading No.	INLET THC lbs/hr	INLET NO lbs/hr	INLET NO_x lbs/hr	INLET CH_4 lbs/hr	OUTLET THC lbs/hr	OUTLET NO lbs/hr	OUTLET NO_x lbs/hr	OUTLET CH_4 lbs/hr	August, 1973 Time
1	9.02	--	.00697		1.19	.0483	.292		11:30
2	10.3	--	.00668		1.23	.0483	.291		11:45
3	9.02	--	.00755	.0303	1.08	.0493	.301	.293	12:00
4	7.58	--	.00726		1.02	.0493	.298		12:15
5	4.02	--	.00712		1.08	.0493	.291		12:30
6	4.27	--	.00799		1.01	.0455	.334		12:45
7	6.70	.00426	.00654		1.02	.0521	.360		13:00
8	6.69	.00377	.00578		0.960	.0557	.287	.122	13:15
9	8.01	.00369	.00566	.0262	0.332	.123	.428		13:30
10	7.59	.00320	.00491		0.442	.102	.402		13:45
11	9.28	.00410	.00692		0.591	.0738	.453		14:00
12	8.92	.0034	.00566		0.997	.0533	.352		14:15
13	8.46	.00213	.00365	.0219	0.923	.0492	.314	.306	14:30
14	8.92	.00427	.00654		1.03	.0312	.312		14:45
15	11.1	.00427	.00775		1.08	--	--		15:00
16	11.1	.00331	.00735		1.12	--	--		15:15
17	10.9	.00549	.00949	.0186	1.06	--	--	.418	15:30
18	9.97	.00479	.00761		1.20	.0392	.251		15:45
19	7.11	.00392	.00788		1.18	.0418	.259		16:00
20	7.32	--	--		1.07	.0418	.258		16:15
21	9.59	.00206	.00437		1.14	.0471	.290		16:30
22	8.54	.00364	.00557	.00523	1.12	.0442	.316	.487	16:45
23	6.95	.00285	.00482		1.05	.0481	.324		17:00
24	8.02	.00138	.00241		0.848	.0589	.339		17:15
25	6.95	.00373	.00572		0.956	--	--		17:30
26	8.02	.00255	.00392	.0104	0.993	--	--	.424	17:45
27	7.31	.00334	.00512		1.01	.0442	.301		18:00
28	7.47	.00334	.00512		1.03	.0481	.301		18:15
29	--	--	--		1.09	.0458	.301		18:30
30	7.11	.00449	.00688		1.15	.0468	.301		18:45
31	7.21	.00318	.00488	.00998	--	--	--	.384	19:00
32	9.13	.00243	.00373		--	--	--		19:15
33	9.80	.00262	.00402		1.03	.0514	.288		19:30

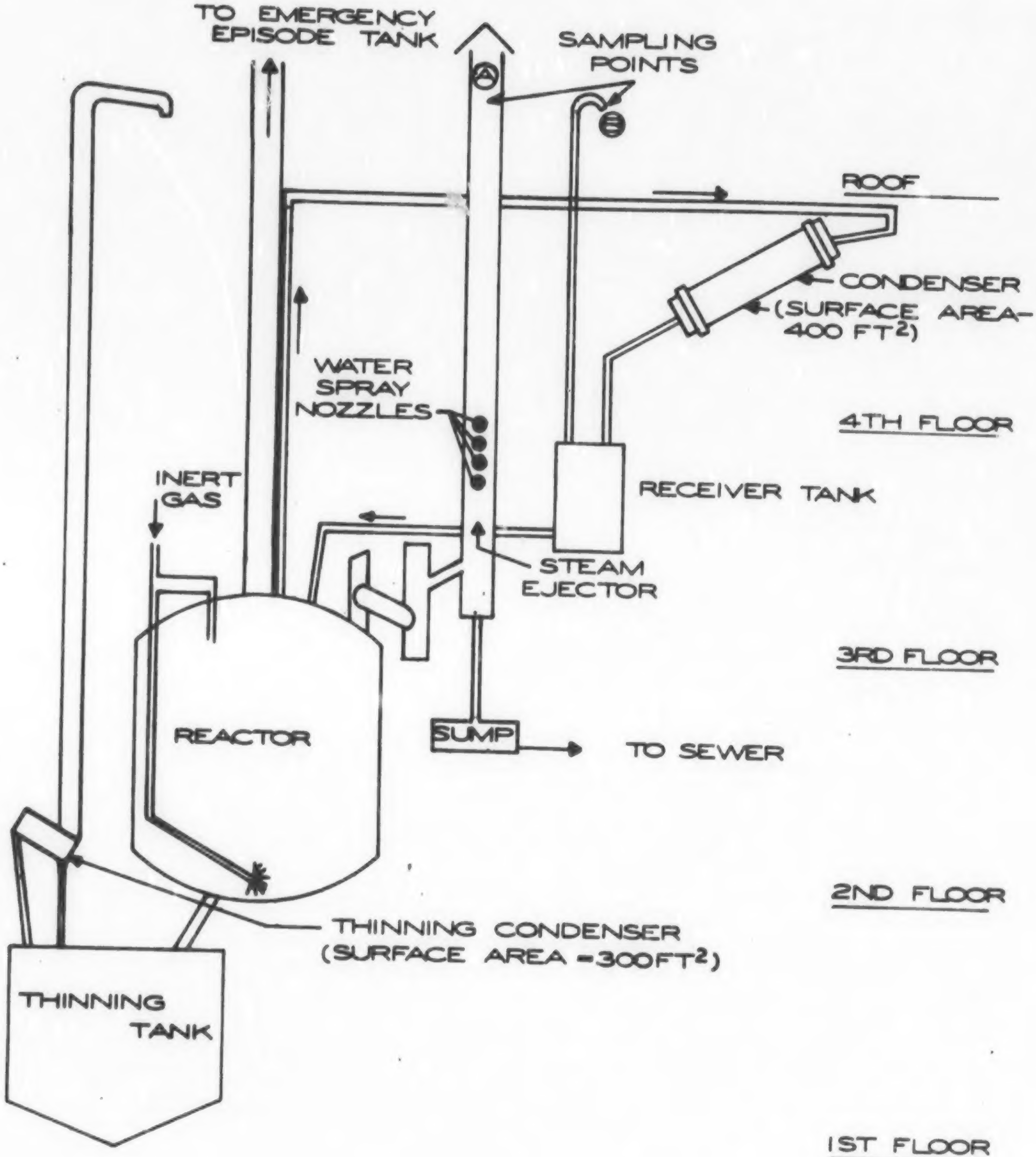
TABLE D-17 THERMAL AFTERBURNER RAW DATA (CONTIN.)

Reading No.	INLET THC lbs/hr	INLET NO lbs/hr	INLET NO_x lbs/hr	INLET CH_4 lbs/hr	OUTLET THC lbs/hr	OUTLET NO lbs/hr	OUTLET NO_x lbs/hr	OUTLET CH_4 lbs/hr	August, 1973 Time
34	10.2	.00299	.00459		0.995	.0514	.294		19:45
35	10.3	.00340	.00521	.00518	1.17	.0562	.335	.388	20:00
36	10.6	.00194	.00327		0.895	.0456	.335		20:15
37	11.3	--	--		0.839	.0805	.347		20:30
38	10.5	.00281	.00431		0.970	.0757	.344		20:45
39	7.91	.00301	.00461		0.951	.0776	.339		21:00
40	8.15	.00291	.00476		0.914	.0679	.387		21:15
AVG.	8.50	.00323	.00572	.0160	0.994	.0531	.322	.352	



REACTOR # 3 & # 4

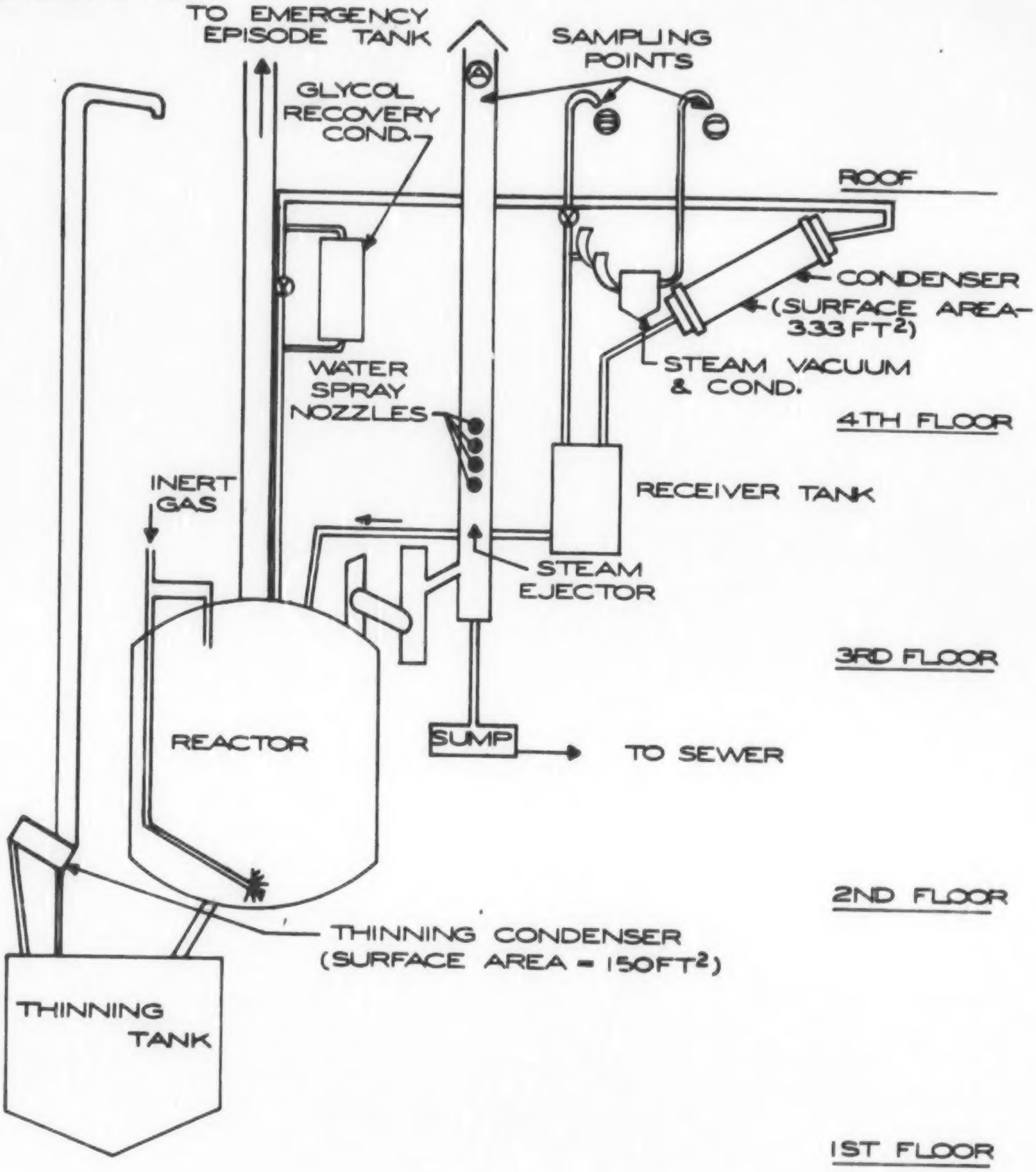
FIGURE D-1



REACTOR # 2

FIGURE D-2

SRL 1372 01 1173



REACTOR #8

FIGURE D-3